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New Synthesis of Known Herbicides Based on Aryloxyalkanoic Acids

L. R. Latypova[a], **Sh. M. Salikhov**[a],* **Yu. V. Legostaeva**[a], **R. N. Khusnitdinov**[a], **G. Yu. Ishmuratov**[a], and **I. B. Abdrakhmanov**[a]

[a] *Institute of Chemistry, Ufa Federal Research Center, Russian Academy of Sciences,*
pr. Oktyabrya 71, Ufa, 450054 Bashkortostan, Russia
**e-mail: Salikhov@anrb.ru*

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Abstract—A new version has been proposed for the synthesis of analogs of the known herbicides mecoprop (MCPP) and dichlorprop (2,4-DP) by ozonolysis of chloro derivatives of (pent-3-en-2-yloxy)benzene.

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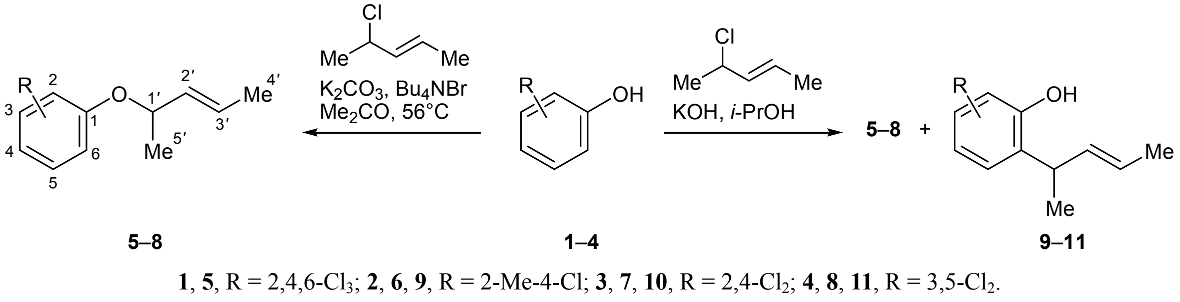
Selective herbicides based on aryloxyalkanoic acids have been thoroughly studied, and they have been widely used for plant protection, especially for the protection of crops [1–4]. However, their preparation is fairly difficult due to multistep procedures of synthesis and low accessibility of required components [5, 6]. This prompted us to study the synthesis of chloro derivatives of (pent-3-en-2-yloxy)benzene and their transformations under ozonolysis conditions with the goal of obtaining the known herbicides mecoprop (MCPP) and dichlorprop (2,4-DP), as well as their analogs [7].

Chlorinated (pent-3-en-2-yloxy)benzenes **5**–**8** were synthesized by heating 4-chloropent-2-ene with the corresponding chlorophenol in the presence of 0.1 equiv of tetrabutylammonium bromide and 2 equiv of potassium carbonate in boiling acetone [8] or 3 equiv of potassium hydroxide in propan-2-ol [9]. The reaction in the presence of KOH was accompanied by Claisen rearrangement, so that mixtures of **5**–**8** and *o*-(pent-3-en-2-yl)chlorophenols **9**–**11** were formed (Scheme 1).

Ozonolysis of olefins provides efficient highly selective introduction of oxygen-containing functionalities into organic molecules [10]; intermediate ozonolysis products (peroxides) are commonly decomposed by treatment with H_2O_2–SeO_2 [11], $NH_2C(O)NHNH_2\cdot HCl$ [12], Me_2S [13], or $NaBH_4$ [11].

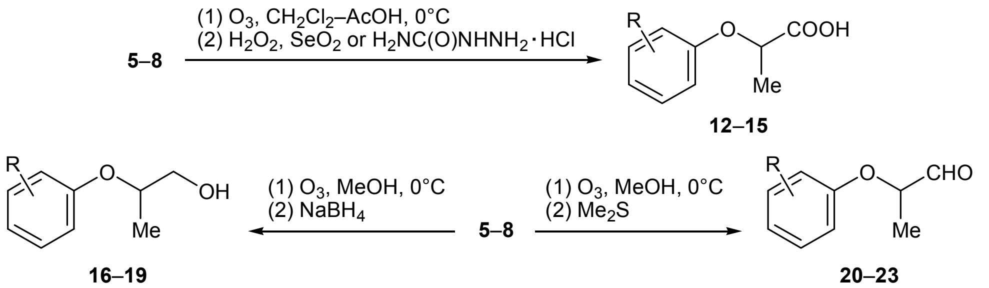
The ozonolysis of **5**–**8** was carried out in the system methylene chloride–acetic acid at 0°C with subsequent oxidation with hydrogen peroxide in the presence of a catalytic amount of selenium dioxide or treatment of peroxides with semicarbazide hydrochloride. We thus obtained 2-(chloroaryloxy)propanoic acids **12**–**15** in 39–86% yield (Scheme 2). When the peroxide ozonolysis products of compounds **5**–**8** were reduced with $NaBH_4$ in methanol at 0°C, we isolated from the reaction mixtures alcohols **16**–**19**, while the reduction with dimethyl sulfide afforded aldehydes **20**–**23** (Scheme 2).

Scheme 1.



1, **5**, R = 2,4,6-Cl_3; **2**, **6**, **9**, R = 2-Me-4-Cl; **3**, **7**, **10**, R = 2,4-Cl_2; **4**, **8**, **11**, R = 3,5-Cl_2.

Scheme 2.



12, **16**, **20**, R = 2,4,6-Cl_3; **13**, **17**, **21**, R = 2-Me-4-Cl; **14**, **18**, **22**, R = 2,4-Cl_2; **15**, **19**, **23**, R = 3,5-Cl_2.

The proposed scheme of synthesis of 2-phenoxypropanoic acid derivatives **12**–**15** can be regarded as an alternative approach to such known crop-selective herbicides as mecoprop (**13**, MCCP) and dichlorprop (**14**, 2,4-DP).

EXPERIMENTAL

The NMR spectra were recorded at the *Khimiya* Joint Center (Ufa Institute of Chemistry, Russian Academy of Sciences) on a Bruker Avance III spectrometer at 500 MHz for ^{1}H and 125.47 MHz for ^{13}C; $CDCl_3$ was used as solvent. Analytical thin-layer chromatography was performed on Sorbfil PTSKh-AF-A plates manufactured by *Sorbpolimer* closed corporation (Krasnodar, Russia). The IR spectra were recorded in the range from 4000 to 200 cm^{-1} on a Specord M80 spectrometer; samples were prepared as films. The mass spectra (electron impact, 70 eV) were obtained on a Thermo Finnigan MAT-95-XP instrument (ion source temperature 200°C). The melting points were measured on a Boetius PHMK 05 melting point apparatus. The elemental compositions were determined using a Euro 2000 CHNS(O) analyzer. The ozonizer efficiency was 40 mmol of O_3 per hour.

***O*-Alkylation of phenols (*general procedure*).** *a*. 4-Chloropent-2-ene, 1.50 g (14.0 mmol), and potassium carbonate, 3.9 g (28.0 mmol), were added to a mixture of 2.0 g (14.0 mmol) of phenol **1**–**4** and 0.50 g (1.4 mmol) of Bu_4NBr in acetone. The mixture was refluxed until the reaction was complete (TLC) and cooled, and the precipitate was filtered off. The filtrate was evaporated, and the residue was purified by column chromatography on Al_2O_3 using petroleum ether as eluent.

b. A mixture of 2.0 g (14.0 mmol) of phenol **1**–**4** and 2.1 g (36.8 mmol) of potassium hydroxide in 50 mL of propan-2-ol was vigorously stirred for 10 min, and 3.8 g (36.8 mmol) of 4-chloropent-2-ene was slowly added. When the reaction was complete (TLC), the precipitate was filtered off, the filtrate was evaporated, and the residue was subjected to column chromatography on Al_2O_3 using petroleum ether as eluent.

2,4,6-Trichloro-1-[(3*E*)-pent-3-en-2-yloxy]benzene (5). Yield 1.10 g (55%) (*a*), 1.06 g (53%) (*b*); oily material, R_f 0.57 (petroleum ether–EtOAc, 5:1). IR spectrum, ν, cm^{-1}: 2983, 1589, 1442, 1255, 831, 671. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.47 d (3H, 5′-H, ^3J = 6.3), 1.60 d.d (3H, 4′-H, ^3J = 6.3, ^4J = 1.0), 4.68 quint (1H, 1′-H, ^3J = 6.3), 5.49 m (1H, 2′-H), 5.61 m (1H, 3′-H), 7.26 s (2H, 3-H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 17.49 ($C^{4'}$), 21.11 ($C^{5'}$), 81.62 ($C^{1'}$), 128.53 (C^3, C^5), 128.71 (C^4), 129.75 ($C^{2'}$), 130.68 (C^2, C^6), 131.11 ($C^{3'}$), 149.19 (C^1). Mass spectrum: *m*/*z* 266.5 $[M + H]^+$. Found, %: C 49.71; H 4.22. $C_{11}H_{11}Cl_3O$. Calculated, %: C 49.75; H 4.18. *M* 265.5625.

4-Chloro-2-methyl-1-[(3*E*)-pent-3-en-2-yloxy]benzene (6). Yield 1.20 g (60%) (*a*), 0.74 g (37%) (*b*); oily material, R_f 0.57 (petroleum ether– EtOAc, 5:1). IR spectrum, ν, cm^{-1}: 2979, 1488, 1244, 869, 661. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.42 d (3H, 5′-H, ^3J = 6.3), 1.69 d.d (3H, 4′-H, ^3J = 6.4, ^4J = 0.9), 2.20 s (3H, CH_3), 4.68 quint (1H, 1′-H, ^3J = 6.3), 5.28 m (1H, 2′-H), 5.68 m (1H, 3′-H), 6.75 d (1H, 6-H, ^3J = 8.6), 7.05 d.d (1H, 5-H, ^3J = 8.6, ^4J = 2.6), 7.11 d (1H, 3-H, ^4J = 2.6). ^{13}C NMR spectrum, δ_C, ppm: 16.35 (CH_3), 17.71 ($C^{4'}$), 21.66 ($C^{5'}$), 70.84 ($C^{1'}$), 114.81 (C^6), 124.86 (C^4), 126.07 (C^5), 127.23 ($C^{3'}$), 129.64 (C^2), 130.35 (C^3), 132.14 ($C^{2'}$), 154.85 (C^1). Mass spectrum: *m*/*z* 211.7 $[M + H]^+$. Found, %: C 68.45; H 7.20. $C_{12}H_{15}ClO$. Calculated, %: C 68.40; H 7.18. *M* 210.6996.

2,4-Dichloro-1-[(3*E*)-pent-3-en-2-yloxy]benzene (7). Yield 1.14 g (57%) (*a*), 0.66 g (33%) (*b*); oily material, R_f 0.54 (petroleum ether–EtOAc, 5 : 1). IR spectrum, ν, cm^{-1}: 2982, 1475, 1258, 803, 667. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.46 d (3H, 5′-H, $^{3}J = 6.3$), 1.69 d.d (3H, 4′-H, $^{3}J = 6.4$, $^{4}J = 1.0$), 4.71 quint (1H, 1′-H, $^{3}J = 6.3$), 5.52 m (1H, 2′-H), 5.68 m (1H, 3′-H), 6.68 d (1H, 6-H, $^{3}J = 8.8$), 7.12 d.d (1H, 5-H, $^{3}J = 8.8$, $^{4}J = 2.6$), 7.35 d (1H, 3-H, $^{4}J = 2.6$). ^{13}C NMR spectrum, δ_C, ppm: 18.05 (C$^{4'}$), 21.52 (C$^{5'}$), 76.98 (C$^{1'}$), 117.41 (C^{6}), 124.95 (C^{2}), 125.81 (C^{4}), 127.27 (C^{5}), 128.24 (C$^{3'}$), 129.89 (C^{3}), 131.37 (C$^{2'}$), 152.55 (C^{1}). Mass spectrum: *m*/*z* 232.1 $[M + \mathrm{H}]^+$. Found, %: C 57.19; H 5.29. $\mathrm{C_{11}H_{12}Cl_2O}$. Calculated, %: C 57.16; H 5.23. *M* 231.1178.

3,5-Dichloro-1-[(3*E*)-pent-3-en-2-yloxy]benzene (8). Yield 1.10 g (55%) (*a*), 0.76 g (38%) (*b*); oily material, R_f 0.51 (petroleum ether–EtOAc, 5 : 1). IR spectrum, ν, cm^{-1}: 2979, 1589, 1444, 965, 855, 670. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.41 d (3H, 5′-H, $^{3}J = 6.3$), 1.72 d.d (3H, 4′-H, $^{3}J = 6.4$, $^{4}J = 1.0$), 4.72 quint (1H, 1′-H, $^{3}J = 6.3$), 5.51 m (1H, 2′-H), 5.72 m (1H, 3′-H), 6.81 d (2H, 2-H, 6-H, $^{4}J = 1.7$), 6.93 t (1H, 4-H, $^{4}J = 1.7$). ^{13}C NMR spectrum, δ_C, ppm: 17.73 (C$^{4'}$), 21.45 (C$^{5'}$), 75.28 (C$^{1'}$), 114.98 (C^{2}, C^{6}), 120.74 (C^{4}), 128.18 (C$^{2'}$), 131.15 (C$^{3'}$), 135.13 (C^{3}, C^{5}), 159.17 (C^{1}). Mass spectrum: *m*/*z* 232.1 $[M + \mathrm{H}]^+$. Found, %: C 57.18; H 5.28. $\mathrm{C_{11}H_{12}Cl_2O}$. Calculated, %: C 57.16; H 5.23. *M* 231.1178.

4-Chloro-2-methyl-6-[(3*E*)-pent-3-en-2-yl]phenol (9). Yield 0.38 g (19%), oily material, R_f 0.58 (petroleum ether–EtOAc, 10 : 1). IR spectrum, ν, cm^{-1}: 3488, 2967, 1457, 1190, 971, 741. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.37 d (3H, 5′-H, $^{3}J = 6.9$), 1.74 d.d (3H, 4′-H, $^{3}J = 5.9$, $^{4}J = 1.0$), 2.21 s (3H, $\mathrm{CH_3}$), 3.52 quint (1H, 1′-H, $^{3}J = 6.8$), 5.67 m (2H, 2′-H, 3′-H), 6.95 d (1H, 5-H, $^{4}J = 2.5$), 6.99 d (1H, 3-H, $^{4}J = 2.5$). ^{13}C NMR spectrum, δ_C, ppm: 15.89 ($\mathrm{CH_3}$), 17.88 (C$^{4'}$), 19.21 (C$^{5'}$), 37.45 (C$^{1'}$), 124.85 (C^{4}), 125.10 (C^{5}), 126.40 (C$^{3'}$), 126.54 (C^{2}), 128.54 (C^{3}), 131.51 (C^{6}), 134.48 (C$^{2'}$), 150.88 (C^{1}). Mass spectrum: *m*/*z* 211.7 $[M + \mathrm{H}]^+$. Found, %: C 68.45; H 7.20. $\mathrm{C_{12}H_{15}ClO}$. Calculated, %: C 68.40; H 7.18. *M* 210.6996.

4,6-Dichloro-2-[(3*E*)-pent-3-en-2-yl]phenol (10). Yield 0.34 g (17%), oily material, R_f 0.41 (petroleum ether–EtOAc, 10 : 1). IR spectrum, ν, cm^{-1}: 3495, 2982, 1476, 1220, 987, 739. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.43 d (3H, 5′-H, $^{3}J = 6.9$), 1.68 d.d (3H, 4′-H, $^{3}J = 5.9$, $^{4}J = 1.0$), 4.31 quint (1H, 1′-H, $^{3}J = 6.8$), 5.48 m (1H, 2′-H), 5.86 m (1H, 3′-H), 6.80 m (2H, 4-H, 6-H). ^{13}C NMR spectrum, δ_C, ppm: 17.91 (C$^{4'}$), 17.99 (C$^{5'}$), 38.13 (C$^{1'}$), 116.59 (C^{6}, C^{4}), 125.01 (C$^{2'}$), 132.94 (C$^{1'}$), 133.38 (C^{2}), 133.35 (C^{3}), 135.45 (C^{5}), 153.59 (C^{1}). Mass spectrum: *m*/*z* 232.1 $[M + \mathrm{H}]^+$. Found, %: C 57.19; H 5.20. $\mathrm{C_{11}H_{12}Cl_2O}$. Calculated, %: C 57.16; H 5.23. *M* 231.1178.

3,5-Dichloro-2-[(3*E*)-pent-3-en-2-yl]phenol (11). Yield 0.40 g (20%), oily material, R_f 0.48 (petroleum ether–EtOAc, 10 : 1). IR spectrum, ν, cm^{-1}: 3479, 2929, 1427, 1267, 985, 721. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.31 d (3H, 5′-H, $^{3}J = 6.9$), 1.69 d.d (3H, 4′-H, $^{3}J = 5.9$, $^{4}J = 1.0$), 3.78 quint (1H, 1′-H, $^{3}J = 6.8$), 5.57 m (2H, 2′-H, 3′-H), 7.03 d (1H, 5-H, $^{4}J = 2.5$), 7.18 d (1H, 3-H, $^{4}J = 2.5$). ^{13}C NMR spectrum, δ_C, ppm: 17.95 (C$^{4'}$), 19.77 (C$^{5'}$), 36.07 (C$^{1'}$), 120.41 (C^{4}), 125.19 (C$^{2'}$), 125.19 (C^{3}), 126.52 (C^{5}), 126.65 (C^{2}), 133.82 (C$^{3'}$), 135.22 (C^{6}), 147.55 (C^{1}). Mass spectrum: *m*/*z* 232.1 $[M + \mathrm{H}]^+$. Found, %: C 57.21; H 5.22. $\mathrm{C_{11}H_{12}Cl_2O}$. Calculated, %: C 57.16; H 5.23. *M* 231.1178.

Treatment of peroxide ozonolysis products of compounds 5–8 (*general procedure*). *a*. An ozone–oxygen mixture was bubbled through a solution of 0.4 mmol of compound **5**–**8** in a mixture of 10 mL of methylene chloride and 0.2 mL of acetic acid, cooled to 0°C, until 0.5 mmol of ozone was absorbed. The mixture was purged with argon, 0.1 mL of hydrogen peroxide and 0.01 g (0.09 mmol) of selenium dioxide were added with stirring at 0°C, and the mixture was stirred for 48 h at room temperature. The mixture was diluted with 30 mL of methylene chloride, washed with brine (2 × 15 mL), dried over $\mathrm{MgSO_4}$, and evaporated, and the residue was subjected to silica gel chromatography using petroleum ether–ethyl acetate (3 : 1) as eluent.

b. An ozone–oxygen mixture was bubbled through a solution of 0.4 mmol of compound **5**–**8** in a mixture of 10 mL of methylene chloride and 2.9 mL of acetic acid, cooled to 0°C, until 0.5 mmol of ozone was absorbed. The mixture was purged with argon, 0.2 g (1.4 mmol) of semicarbazide hydrochloride was added with stirring at 0°C, and the mixture was stirred at room temperature until peroxide compounds disappeared (starch–iodine test). The mixture was diluted with 30 mL of methylene chloride, washed with water (3 × 15 mL), dried over $\mathrm{MgSO_4}$, and evaporated, and the residue was subjected to silica gel chromatography using petroleum ether–ethyl acetate (3 : 1) as eluent.

2-(2,4,6-Trichlorophenoxy)propanoic acid (12). Yield 0.06 g (60%) (*a*), 0.05 g (56%) (*b*); yellow crystals, mp 179–180°C, R_f 0.24 (petroleum ether–EtOAc, 2 : 1). IR spectrum, ν, cm^{-1}: 3518, 3081, 1717, 1569, 1471, 1256, 856, 732, 579. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.63 d (3H, 3′-H, ^3J = 6.9), 4.92 q (1H, 2′-H, ^3J = 6.9), 7.27 s (2H, 3-H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 17.96 ($C^{3'}$), 77.48 ($C^{2'}$), 121.61 (C^2, C^6), 121.31 (C^4), 128.08 (C^3, C^5), 146.92 (C^1), 175.07 (C=O). Mass spectrum, *m*/*z*: 270.5 $[M + H]^+$. Found, %: C 40.14; H 2.65. $C_9H_7Cl_3O_3$. Calculated, %: C 40.11; H 2.62. *M* 269.5082.

2-(4-Chloro-2-methylphenoxy)propanoic acid (13). Yield 0.06 g (58%) (*a*), 0.04 g (39%) (*b*); light brown crystals, mp 93–94°C, R_f 0.21 (petroleum ether–EtOAc, 2 : 1). IR spectrum, ν, cm^{-1}: 3508, 2946, 1705, 1493, 1245, 792. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.67 d (3H, 3′-H, ^3J = 6.8), 2.25 s (3H, CH_3), 4.74 q (1H, 2′-H, ^3J = 6.8), 6.64 d (1H, 6-H, ^3J = 8.7), 7.07 d.d (1H, 5-H, ^3J = 8.7, ^4J = 2.4), 7.13 d (1H, 3-H, ^4J = 2.4). ^{13}C NMR spectrum, δ_C, ppm: 16.15 (CH_3), 18.45 ($C^{3'}$), 72.65 ($C^{2'}$), 113.14 (C^6), 126.37 (C^4), 126.37 (C^5), 129.54 (C^2), 130.91 (C^3), 154.14 (C^1), 176.85 (C=O). Mass spectrum: *m*/*z* 215.6 $[M + H]^+$. Found, %: C 55.98; H 5.20. $C_{10}H_{11}ClO_3$. Calculated, %: C 55.96; H 5.17. *M* 214.6452.

2-(2,4-Dichlorophenoxy)propanoic acid (14). Yield 0.05 g (46%) (*a*), 0.04 g (44%) (*b*); light yellow crystals, mp 116–117°C, R_f 0.24 (petroleum ether–EtOAc, 2 : 1). IR spectrum, ν, cm^{-1}: 2955, 1713, 1458, 1243, 798. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.72 d (3H, 3′-H, ^3J = 6.8), 4.78 q (1H, 2′-H, ^3J = 6.8), 6.84 d (1H, 6-H, ^3J = 8.8), 7.17 d.d (1H, 5-H, ^3J = 8.8, ^4J = 2.5), 7.40 d (1H, 3-H, ^4J = 2.5). ^{13}C NMR spectrum, δ_C, ppm: 18.23 ($C^{3'}$), 74.01 ($C^{2'}$), 116.50 (C^6), 124.98 (C^2), 127.66 (C^5), 127.67 (C^4), 130.43 (C^3), 151.80 (C^1), 175.83 (C=O). Mass spectrum: *m*/*z* 236.1 $[M + H]^+$. Found, %: C 46.01; H 3.46. $C_9H_8Cl_2O_3$. Calculated, %: C 45.99; H 3.43. *M* 235.0634.

2-(3,5-Dichlorophenoxy)propanoic acid (15). Yield 0.09 g (86%) (*a*), 0.05 g (54%) (*b*); dark yellow crystals, mp 184–185°C, R_f 0.26 (petroleum ether–EtOAc, 2 : 1). IR spectrum, ν, cm^{-1}: 3520, 2991, 1724, 1574, 1442, 1257, 1093, 802, 670. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.67 d (3H, 3′-H, ^3J = 6.8), 4.77 q (1H, 2′-H, ^3J = 6.8), 6.80 d (2H, 2-H, 6-H, ^4J = 1.6), 7.01 t (1H, 4-H, ^4J = 1.6). ^{13}C NMR spectrum, δ_C, ppm: 18.26 ($C^{3'}$), 72.35 ($C^{2'}$), 114.24 (C^2, C^6), 122.27 (C^4), 135.60 (C^3, C^5), 158.28 (C^1), 176.47 (C=O). Mass spectrum: *m*/*z* 236.1 $[M + H]^+$. Found, %: C 46.03; H 3.43. $C_9H_8Cl_2O_3$. Calculated, %: C 45.99; H 3.43. *M* 235.0634.

Reduction of peroxide ozonolysis products with $NaBH_4$ (*general procedure*). An ozone–oxygen mixture was bubbled through a solution of 0.45 mmol of compound **5–8** in 10 mL of anhydrous methanol, cooled to 0°C, until 0.5 mmol of ozone was absorbed. The mixture was purged with argon, 0.04 g (1.0 mmol) of $NaBH_4$ was added at 0°C, and the mixture was stirred at room temperature until peroxide compounds disappeared (starch–iodine test). The mixture was then treated with 1 mL of 10% acetic acid, the aqueous layer was extracted with chloroform (3 × 10 mL), the extract was dried over $MgSO_4$ and evaporated, and the residue was subjected to silica gel chromatography using petroleum ether–ethyl acetate (7 : 1) as eluent.

2-(2,4,6-Trichlorophenoxy)propan-1-ol (16). Yield 0.09 g (98%), oily material, R_f 0.34 (petroleum ether–EtOAc, 3 : 1). IR spectrum, ν, cm^{-1}: 3385, 2935, 1551, 1446, 1257, 1046, 575. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.32 d (3H, CH_3, ^3J = 6.5), 3.71 d.d (1H, 1′-H, ^2J = 12.0, ^3J = 5.0), 3.82 d.d (1H, 1′-H, ^2J = 12.0, ^3J = 3.0), 4.57 m (1H, 2′-H), 7.34 s (2H, 3-H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 16.18 ($C^{3'}$), 66.05 ($C^{1'}$), 81.07 ($C^{2'}$), 128.29 (C^3, C^5), 129.22 (C^4), 130.11 (C^2, C^6), 148.96 (C^1). Mass spectrum: *m*/*z* 256.5 $[M + H]^+$. Found, %: C 42.35; H 3.57. $C_9H_9Cl_3O_2$. Calculated, %: C 42.30; H 3.55. *M* 255.5247.

2-(4-Chloro-2-methylphenoxy)propan-1-ol (17). Yield 0.08 g (88%), oily material, R_f 0.31 (petroleum ether–EtOAc, 3 : 1). IR spectrum, ν, cm^{-1}: 3383, 2930, 1485, 1246, 1050, 661. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.25 d (3H, 3′-H, ^3J = 6.2), 2.19 s (3H, CH_3), 3.73 d.d (1H, 1′-H, ^2J = 11.7, ^3J = 6.4), 3.77 d.d (1H, 1′-H, ^2J = 11.7, ^3J = 4.1), 4.44 m (1H, 2′-H), 6.81 d (1H, 3-H, ^3J = 8.6), 7.08 d.d (1H, 5-H, ^3J = 8.6, ^4J = 2.6), 7.12 d (1H, 3-H, ^4J = 2.6). ^{13}C NMR spectrum, δ_C, ppm: 15.91 (CH_3), 16.30 ($C^{3'}$), 66.37 ($C^{1'}$), 75.54 ($C^{2'}$), 114.63 (C^6), 125.63 (C^4), 126.43 (C^5), 129.84 (C^2), 130.71 (C^3), 154.37 (C^1). Mass spectrum: *m*/*z* 200.7 $[M + H]^+$. Found, %: C 59.91; H 6.55. $C_{10}H_{13}ClO_2$. Calculated, %: C 59.86; H 6.53. *M* 200.6617.

2-(2,4-Dichlorophenoxy)propan-1-ol (18). Yield 0.09 g (98%), oily material, R_f 0.31 (petroleum ether–EtOAc, 3 : 1). IR spectrum, ν, cm^{-1}: 3374, 2932, 1478, 1261, 1059, 654. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.31 d (3H, 3′-H, ^3J = 6.2), 3.75 m (2H, 1′-H), 4.44 m (1H, 2′-H), 6.93 d (1H, 6-H, ^3J = 8.8), 7.18 d.d (1H, 5-H, ^3J = 8.8, ^4J = 2.5), 7.37 d (1H, 3-H, ^4J = 2.5). ^{13}C NMR spectrum, δ_C, ppm: 15.91 ($C^{3'}$), 66.09 ($C^{1'}$), 77.79 ($C^{2'}$), 117.31 (C^6), 125.2 (C^4), 126.65 (C^2), 127.69 (C^5), 130.13 (C^3), 152.33 (C^1). Mass spectrum: *m*/*z* 222.1 $[M + H]^+$. Found, %: C 48.91; H 4.58.

$C_9H_{10}Cl_2O_2$. Calculated, %: C 48.89; H 4.56. *M* 221.0799.

2-(3,5-Dichlorophenoxy)propan-1-ol (19). Yield 0.09 g (98%), oily material, R_f 0.34 (petroleum ether–EtOAc, 3:1). IR spectrum, ν, cm^{-1}: 3373, 2935, 1589, 1440, 1259, 1054, 833, 671. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.25 d (3H, 3′-H, ^3J = 6.3), 3.65 m (2H, 1′-H), 4.43 m (1H, 2′-H), 6.81 s (2H, 2-H, 6-H), 6.93 s (1H, 4-H). ^{13}C NMR spectrum (125.47 MHz, $CDCl_3$), δ_C, ppm: 15.59 ($C^{3'}$), 65.80 ($C^{1'}$), 75.64 ($C^{2'}$), 114.84 (C^2, C^6), 121.27 (C^4), 135.35 (C^3, C^5), 158.85 (C^1). Mass spectrum: *m*/*z* 222.1 $[M + H]^+$. Found, %: C 48.90; H 4.59. $C_9H_{10}Cl_2O_2$. Calculated, %: C 48.89; H 4.56. *M* 221.0799.

Treatment of peroxide ozonolysis products with dimethyl sulfide (*general procedure*). An ozone–oxygen mixture was bubbled through a solution of 0.45 mmol of compound **5**–**8** in 10 mL of anhydrous methanol, cooled to 0°C, until 0.5 mmol of ozone was absorbed. The mixture was purged with argon, 0.05 mL of dimethyl sulfide was added with stirring at 0°C, and the mixture was stirred at room temperature until peroxide compounds disappeared (starch–iodine test). The solvent was distilled off, the residue was dissolved in 10 mL of chloroform, the solution was washed with a saturated aqueous solution of sodium hydrogen carbonate (2 × 5 mL) and with brine (2 × 5 mL), dried over $MgSO_4$, and evaporated, and the residue was subjected to silica gel chromatography using petroleum ether–ethyl acetate (6:1).

2-(2,4,6-Trichlorophenoxy)propanal (20). Yield 0.09 g (88%), oily material, R_f 0.37 (petroleum ether–EtOAc, 5:1). IR spectrum, ν, cm^{-1}: 3298, 2939, 1733, 1435, 1258, 1054, 577. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.48 d (3H, 3′-H, ^3J = 7.0), 4.59 m (1H, 2′-H), 7.24 s (2H, 3-H, 5-H), 9.98 d (1H, CHO, ^3J = 1.5). ^{13}C NMR spectrum, δ_C, ppm: 17.45 ($C^{3'}$), 83.89 ($C^{2'}$), 129.01 (C^3, C^5), 129.89 (C^2, C^6), 131.08 (C^4), 148.94 (C^1), 200.83 (CHO). Mass spectrum: *m*/*z* 254.5 $[M + H]^+$. Found, %: C 42.66; H 2.79. $C_9H_7Cl_3O_2$. Calculated, %: C 42.64; H 2.78. *M* 253.5088.

2-(4-Chloro-2-methylphenoxy)propanal (21). Yield 0.08 g (80%), oily material, R_f 0.25 (petroleum ether–EtOAc, 5:1). IR spectrum, ν, cm^{-1}: 3444, 2927, 1739, 1489, 1245, 1081, 663. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.49 d (3H, 3′-H, ^3J = 6.9), 2.26 s (3H, CH_3), 4.59 m (1H, 2′-H), 6.61 d (1H, 6-H, ^3J = 8.7), 7.08 d.d (1H, 5-H, ^3J = 8.7, ^4J = 2.4), 7.16 d (1H, 3-H, ^4J = 2.4), 9.71 d (1H, CHO, ^3J = 1.8). ^{13}C NMR spectrum, δ_C, ppm: 15.56 ($C^{3'}$), 16.21 (CH_3), 78.34 ($C^{2'}$), 113.20 (C^6), 126.32 (C^2), 126.44 (C^5), 129.45 (C^4), 131.03 (C^3), 154.07 (C^1), 201.93 (CHO). Mass spectrum: *m*/*z* 199.6 $[M + H]^+$. Found, %: C 60.49; H 5.60. $C_{10}H_{11}ClO_2$. Calculated, %: C 60.46; H 5.58. *M* 198.6458.

2-(2,4-Dichlorophenoxy)propanal (22). Yield 0.09 g (94%), oily material, R_f 0.38 (petroleum ether–EtOAc, 5:1). IR spectrum, ν, cm^{-1}: 3346, 2939, 1740, 1478, 1263, 1060, 655. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.51 d (3H, 3′-H, ^3J = 6.9), 4.61 d.q (1H, 2′-H, ^3J = 6.9, 1.6), 6.79 d (1H, 6-H, ^3J = 8.8), 7.15 d.d (1H, 5-H, ^3J = 8.8, ^4J = 2.5), 7.39 d (1H, 3-H, ^4J = 2.5), 9.74 d (1H, CHO, ^3J = 1.6). ^{13}C NMR spectrum, δ_C, ppm: 15.79 ($C^{3'}$), 79.93 ($C^{2'}$), 116.55 (C^6), 125.01 (C^2), 127.49 (C^4), 127.71 (C^5), 130.49 (C^3), 151.88 (C^1), 201.88 (CHO). Mass spectrum: *m*/*z* 220.1 $[M + H]^+$. Found, %: C 49.36; H 3.69. $C_9H_8Cl_2O_2$. Calculated, %: C 49.34; H 3.68. *M* 219.064.

2-(3,5-Dichlorophenoxy)propanal (23). Yield 0.08 g (81%), oily material, R_f 0.5 (petroleum ether–EtOAc, 3:1). IR spectrum, ν, cm^{-1}: 3394, 2937, 1739, 1572, 1443, 1258, 1078, 670. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.50 d (3H, 3′-H, ^3J = 6.9), 4.62 d.q (1H, 2′-H, ^3J = 6.9, ^3J = 1.3), 6.79 d (2H, 2-H, 6-H, ^4J = 1.6), 7.01 t (1H, 4-H, ^4J = 1.6), 9.68 d (1H, CHO, ^3J = 1.3). ^{13}C NMR spectrum, δ_C, ppm: 15.28 ($C^{3'}$), 78.28 ($C^{2'}$), 114.36 (C^2, C^6), 122.24 (C^4), 135.72 (C^3, C^5), 158.23 (C^1), 200.46 (CHO). Mass spectrum: *m*/*z* 220.1 $[M + H]^+$. Found, %: C 49.37; H 3.68. $C_9H_8Cl_2O_2$. Calculated, %: C 49.34; H 3.68. *M* 219.064.

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REFERENCES

1. Kulikova, N.A. and Lebedeva, G.F., *Gerbitsidy i ekologicheskie aspekty ikh primeneniya* (Herbicides and Environmental Aspects of Their Application), Moscow: LIBROKOM, 2010.
2. Zinchenko, V.A., *Khimicheskaya zashchita rastenii: sredstva, tekhnologiya i ekologicheskaya bezopasnost'* (Chemical Plant Protection: Means, Technologies, and Environmental Safety), Moscow: KolosS, 2012.
3. Mel'nikov, N.N., Novozhilov, K.V., and Belan, S.R., *Pestitsidy i regulyatory rosta rastenii. Spravochnik* (Pesticides and Plant Growth Regulators. Reference Book), Moscow: Khimiya, 1995.
4. *The Pesticide Manual Incorporating the Agrochemicals Handbook*, Tomlin, C., Ed., Farnham UK: British Crop Protection Council, 1994, 10th ed.
5. Torikov, V.E., *Agrobiznes*, 2006, no. 2, p. 78.

6. Strokin, V.L., *Plodorodie*, 2009, no. 4, p. 35.
7. Ganiev, M.M., *Khimicheskie sredstva zashchity rastenii* (Chemical Means for Plant Protection), St. Petersburg: Lan', 2013.
8. Kazemi, M., Noori, Z., Kohzadi, H., and Sayadi, M., *Iran. Chem. Commun.*, 2013, vol. 1, p. 43.
9. Timofeeva, S.A., Zlotskii, S.S., Grudnikov, I.B., and Yumakaeva, Yu.M., *Bashk. Khim. Zh.*, 2010, vol. 17, no. 3, p. 25.
10. Odinokov, V.N. and Tolstikov, G.A., *Russ. Chem. Rev.*, 1981, vol. 50, no. 7, p. 636.
11. Ishmuratov, G.Yu., Legostaeva, Yu.V., Botsman, L.P., and Tolstikov, G.A., *Russ. J. Org. Chem.*, 2010, vol. 46, no. 11, p. 1593.
12. Raskil'dina, G.Z., Legostaeva, Y.V., Garifullina, L.R., Sultanova, R.M., Ishmuratov, G.Y., and Zlotskii, S.S., *Lett. Org. Chem.*, 2016, vol. 13, p. 652.
13. Amarante, G.W., *Synlett*, 2009, no. 1, p. 155.