Synthesis and Bioactivity of Quinone Mono- and Dioxime Salts

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Abstract: Eliminating all kinds of harmful organisms is an important task in agriculture, food production, and human life. Quinone oximes and their salts are good bioactive compounds to attain this aim. The alkali metal salts of quinone mono- and dioxime have been synthesized by the reaction of the corresponding quinone oxide with alkali metal hydroxide. The divalent metal salts have been obtained in two stages. The first stage is the synthesis of the sodium salt of the quinone oxime. The second step is the reaction of the latter with a divalent metal salt. Copper and zinc salts of [(4-oxocyclohexa-2,5-dien-1-ylidene)amino]oxidanide have the highest insecticidal activity against the housefly and rice weevil. The death index is 90–100%. Copper [(2-methyl-4-oxo-5-(propan-2-yl)cyclohexa-2,5-dien-1-ylidene)amino]oxidanide shows good activity against Phytophthora infestans. Inhibition of the growth and development of the Phytophthora infestans is 80%.

Keywords: quinone; quinone monooxime; quinone dioxime; alkali metal salt; copper salt; zinc salt; insecticide; fungicide.

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1. Introduction

Eliminating all kinds of harmful organisms is an important task in agriculture, food production, and human life. Rice weevils are harmless to human, but they feed on cereals, flour, and cornmeal. The big problem is to keep them out of processes and crops. Aphids are the main pests in agriculture, causing large crop yield losses [1]. Because arachnid mites feed on the plant leaves, they cause a lot of crop losses [2]. Houseflies are carriers of human and animal diseases caused by protozoa, viruses, bacteria, and pathogens. These pathogens are transported by mouthparts, feces, gut, mouth saliva, and the surface of its body. They usually spread harmful pathogens that come into contact with animals and/or human [3].

Various insecticides are used to control pests, but over time, insects become resistant to them [4–9]. Thus, new insecticides against rice weevil [10, 11], aphid [5, 12], arachnid mite [13], and housefly [3, 14, 15] are being sought. And this task is relevant.

Many of the plant diseases depend on microorganisms. One type of plant can be infected by a few microbial phytopathogen parasitizes.

Fusarium moniliforme produces mycotoxins that cause many diseases. These mycotoxins are common harmful substances found in plants, food, and feed. The presence of mycotoxins is a risk for animal and human health [16]. Xanthomonas is a genus of bacterial
plant pathogens that cause many diseases in economically important crops [17], for example, cotton gummosis. The fungus *Penicillium cyclopium* affects cereal products. It produces mycotoxins that affect various crops [18].

It is relevant to use the bioactive substances for the protection of agricultural raw materials and plant products (feed, food) from microorganisms producing mycotoxins, in particular for the prevention of the formation of fungal biofilms [19–22].

Quinone oximes and their salts are good synthons for the synthesis of new biologically active derivatives [23, 24]. Different quinone oximes and their derivatives were synthesized earlier [25, 26]. Quinoid compounds have high persicidal activity [27, 28]. Metals, their complexes and salts are widely used in the applied biological sciences and are bioactive agents [29–31]. Various salts of quinone mono- and dioximes have been synthesized before [32], but their biologic activity has not been studied.

Thus, the purpose of our work is to synthesize new quinone mono- and dioxime salts, which could be used as anti-nematode, insecticidal, and fungicidal agents. We also studied the biologic activity of oxime salts synthesized previously.

### 2. Materials and Methods

#### 2.1. General experimental details.

The $^1$H NMR spectra were measured on the Varian VXR-300 spectrometer (300 MHz) using TMS as an internal standard. DMSO-d$_6$ was used as a solvent. The IR spectra were recorded on a UR-20 spectrometer in KBr. The purity of the reaction products and initial compounds was determined by TLC on Silufol UV-254 plates. Acetone was used as a solvent. A mixture of ethanol and chloroform (1:10) was used as eluent. The spots were developed under UV light. The melting points were uncorrected.

Quinone monoximes 1a-d were synthesized by nitrosation of the corresponding phenols by the procedures reported in [33, 34]. Quinone dioxime 6 was obtained by the method described in [35].

**Alkali metal salts of [(4-oxocyclohexa-2,5-dien-1-ylidene)amino]oxidanide** 2a-d, 3-(oxidoiminio)-6-oxocyclohexa-1,4-diene-1-carboxylate 4a-c and N,N'-cyclohexa-2,5-diene-1,4-diylidenedithydroxylamine 7a-c (general procedure). 0.1 or 0.2 mole of alkali metal hydroxide was added to the mixture of 100 ml of methanol and 0.1 mole of quinone oxime 1a-d or oxime 1e, 6, respectively. The mixture was refluxed until the initial compounds were completely dissolved. After that, it was cooled and slowly poured with stirring into 700 ml of diethyl ether. The precipitate was filtered off under low pressure, washed with diethyl ether, and dried. The products were colored crystalline substances, which decomposed by heating in a wide temperature range.

**Alkali metal salts of** 10a-d, 13 were obtained by the analogous procedure.

Characteristics of metal salts 2a-d, 7a-c, 10a-d, 13 correspond to literary data [32].

**Dilithium** 3-(oxidoiminio)-6-oxocyclohexa-1,4-diene-1-carboxylate 4a. Yield 72%; deep-brown crystals; m.p. >200°C (decomposition). NMR $^1$H (δ, ppm): Z-isomer, 6.08 (d, 1H, H$^3$, J 8.8 Hz), 7.82 (k, 1H, H$^4$, J 8.8, 2.6 Hz), 7.85 (d, 1H, H$^2$, J 2.6 Hz); E-isomer, 5.89 (d, 1H, H$^5$, J 9.6 Hz), 6.72 (k, 1H, H$^4$, J 9.6, 3.0 Hz), 6.77 (d, 1H, H$^2$, J 3.0 Hz). Anal. Calcd. For C$_9$H$_{13}$Li$_2$NO$_4$: C, 46.97; N 7.83%. Found: C, 46.58; N, 7.79%.

**Disodium** 3-(oxidoiminio)-6-oxocyclohexa-1,4-diene-1-carboxylate 4b. Yield 97%; yellow-brown crystals; m.p. >200°C (decomposition). NMR $^1$H (δ, ppm): Z-isomer, 6.06 (d,
1H, H², J 8.8 Hz), 7.83 (k, 1H, H⁴, J 8.8, 2.6 Hz), 7.83 (d, 1H, H², J 2.6 Hz); E-isomer, 5.91 (d, 1H, H³, J 9.6 Hz), 6.74 (k, 1H, H⁴, J 9.6, 3.0 Hz), 6.76 (d, 1H, H², J 3.0 Hz). Anal. Calcd. For C₇H₅N₂O₄: C, 39.83; N 6.64%. Found: C, 40.02; N, 5.59%.

Divalent metal salts of [(4-oxocyclohexa-2,5-dien-1-ylidene)amino]oxidanide 3a-h, 3-(oxidoimino)-6-oxocyclohexa-1,4-diene-1-carboxylate 5a, b and N,N'-cyclohexa-2,5-diene-1,4-diylidenedihydroxylamine 8 (general procedure). 0.1 Mole of quinone monooxime 1a-e or quinone dioxime 6 was dissolved by heating up to 60–70 °C in 250 ml of water containing 0.1 (for compounds 1a-d) or 0.2 (for compounds 1e, 6) mole of sodium hydroxide. The colored hot solution was filtered. Solution of the corresponding divalent metal salt (sulfate, nitrate, or chloride) in a minimal amount of water was slowly added to the filtrate with stirring. The mixture was cooled and kept for 24 h. The precipitate was filtered off under low pressure, washed with water and methanol, and dried. The products were colored crystalline substances, which decomposed by heating in a wide temperature range.

Copper 3-(oxidoimino)-6-oxocyclohexa-1,4-diene-1-carboxylate 5a. Yield 95%; black crystals; m.p. >200°C (decomposition). Anal. Calcd. For C₇H₅CuO₄: C, 36.77; N 6.13%. Found: C, 36.62; N, 6.22%.

Zinc 3-(oxidoimino)-6-oxocyclohexa-1,4-diene-1-carboxylate 5b. Yield 98%; green crystals; m.p. >200°C (decomposition). Anal. Calcd. For C₇H₅ZnO₄: C, 36.47; N 6.08%. Found: C, 36.58; N, 6.18%.

Divalent metal salts of 11, 14 were obtained by the analogous procedure. Characteristics of metal salts 3a-h, 8, 11, 14 correspond to literary data [32].

2.2. Biological studies.

Biologic activities of compounds were determined in the biological testing laboratory in the Kiev Research Institute Sinteko, OJSC, Ukraine.

3. Results and Discussion

Alkali metal salts of [(4-oxocyclohexa-2,5-dien-1-ylidene)amino]oxidanide 2a-d were synthesized in the reaction of 4-(hydroxyimino)cyclohexa-2,5-dien-1-one 1a-d with corresponding alkali metal hydroxide (Scheme 1). In order to synthesize divalent metal salts 3a-h, the reaction was carried out in two stages. First, the sodium salt of corresponding oxidanide was obtained, which was converted into the desired product by reaction with a divalent metal salt solution.

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Me=Cu (b), R¹=H, R²=CH₃, Me=Cu (c), R¹=i-Pr, R²=CH₃, Me=Cu (d), R¹=R²=H, Me=Zn (e), R¹=CH₃, R²=H, Me=Zn (f), R¹=H, R²=CH₃, Me=Zn (g), R¹=i-Pr, R²=CH₃, Me=Zn (h).

**Scheme 1.** Synthesis of the metal salts of [(4-oxocyclohexa-2,5-dien-1-ylidene)amino]oxidanide 2a-d, 3a-h.

Metal salts of 3-(oxidoimino)-6-oxocyclohexa-1,4-diene-1-carboxylate 4a-c, 5a, b were obtained by the same procedure (Scheme 2).

4: Me=Li (a), Na (b), K (c); 5: Me=Cu (a), Zn (b).

**Scheme 2.** Synthesis of the metal salts of 3-(oxidoimino)-6-oxocyclohexa-1,4-diene-1-carboxylate 4a-c, 5a, b.

The structures of compounds 4a-c, 5a, b were determined by elemental analysis and IR and NMR ¹H spectra. In IR spectra of compounds 4a-c, 5a, b the absorption bands were observed in the region of 1580–1665 cm⁻¹ (C=O) and 1500–1610 cm⁻¹ (C=N). The salts 5a, b were insoluble in organic solvents; therefore, their structures were studied with alkali metal derivatives, which were soluble in many organic solvents.

Alkali metal salts of {cyclohexa-2,5-diene-1,4-diylidenebis[(E)azanylylidene]}-bis(oxidanide) 7a-c were synthesized by reaction of N,N'-cyclohexa-2,5-diene-1,4-diylidenedihydroxylamine 6 with corresponding alkali metal hydroxide (Scheme 3).

7: Me=Li (a), Na (b), K (c).

**Scheme 3.** Synthesis of the metal salts of {cyclohexa-2,5-diene-1,4-diylidenebis[azanylylidene]}bis(oxidanide) 7a-c, 8.

The divalent metal salt 8 was obtained in two stages: 1) the synthesis of sodium salt 7b, 2) reaction of sodium salt 7b with a divalent metal salt.

We also synthesized naphthalene derivatives of quinone oximes, since various naphthalene derivatives show high biologic activity [36].

Alkali metal salts of [(1-oxonaphthalen-2(1H)-ylidene)amino]oxidanides 10a-d, 11 and [(2-oxonaphthalen-1(2H)-ylidene)amino]oxidanide 13, 14 were synthesized by reaction of corresponding 2-(hydroxyimino)naphthalen-1(2H)-ones 9a,b or 1-(hydroxyimino)naphthalen-2(1H)-one 12 with alkali metal hydroxide (scheme 4). The copper salts 11 and 12 were also obtained in two stages.

The metal salts of quinone mono- and dioximes 2a-d, 3a-h, 4a-c, 5a, b, 7a-c, 8, 10a-d, 11, 13, 14 were tested for insecticidal and anti-nematode activity.

In order to study the insecticidal activity of these compounds, we used aqueous solutions of the alkali metal salts and aqueous suspensions of the copper and zinc salts. The concentration of the tested compound in the solution was 0.5% in tests of weevils and flies, 0.01% in tests of aphids, and 0.1% in tests of mites. We studied the action of these solutions on house flies (Musca domestica), rice weevils (Sitophilus oryzae), arachnid mites (Tetranychus urticae), and black beet aphids (Aphis fabae Scopoli).

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In the study of anti-nematode activity, the concentration of the tested compound was 80 mg/kg under soil application.

The results of biological activity studies are shown in Table 1.

![Chemical structures and reactions](https://doi.org/10.33263/BRIAC105.61486156)

**Scheme 4.** Synthesis of the metal salts of [(1-oxonaphthalen-2(1H)-ylidene)amino]oxidanides 10a-d, 11 and [(2-oxonaphthalen-1(2H)-ylidene)amino]oxidanide 13, 14.

**Table 1.** The test results of insecticidal and anti-nematode activities of compounds 2a-d, 3a-h, 4a-c, 5a, b, 7a-c, 8, 10a-d, 11, 13, 14.

| Compound number | **Musca domestica** | **Sitophilus oryzae** | **Tetranychus urticae** | **Aphis fabae Scopoli** | **The reduction of gall formation on cucumber roots, %** |
|-----------------|--------------------|-----------------------|------------------------|------------------------|-----------------------------------------------------|
| 2a              | 0                  | 0                     | 0                      | 16                     | 0                                                   |
| 2b              | 0                  | 18                    | 0                      | 0                      | 0                                                   |
| 2c              | 0                  | 32                    | 0                      | 6                      | 0                                                   |
| 2d              | 0                  | 32                    | 0                      | 6                      | 0                                                   |
| 3a              | 4                  | 11                    | 30                     | 0                      | 0                                                   |
| 3b              | 100                | 62                    | 5                      | 14                     | 73                                                  |
| 3c              | 0                  | 0                     | 26                     | 20                     | 0                                                   |
| 3d              | 8                  | 3                     | 26                     | 3                      | 0                                                   |
| 3e              | 5                  | 18                    | 0                      | 0                      | 0                                                   |
| 3f              | 96                 | 100                   | 13                     | 0                      | 0                                                   |
| 3g              | 100                | 100                   | 18                     | 19                     | 0                                                   |
| 3h              | 90                 | 100                   | 10                     | 3                      | 6                                                   |
| 4a              | 0                  | 68                    | 0                      | 0                      | 0                                                   |
| 4b              | 0                  | 44                    | 4                      | 7                      | 9                                                   |
| 4c              | 0                  | 35                    | 2                      | 10                     | 0                                                   |
| 5a              | 100                | 41                    | 3                      | 14                     | 9                                                   |
| 5b              | 0                  | 42                    | 14                     | 0                      | 0                                                   |
| 5c              | 0                  | 76                    | 0                      | 0                      | 0                                                   |
| 5d              | 0                  | 62                    | 0                      | 0                      | 0                                                   |
| 6c              | 0                  | 39                    | 60                     | 13                     | 0                                                   |
| 8               | 0                  | 11                    | 21                     | 17                     | 0                                                   |
| 10a             | 0                  | 44                    | 5                      | 0                      | 0                                                   |
| 10b             | 0                  | 60                    | 11                     | 7                      | 39                                                  |
| 10c             | 0                  | 21                    | 7                      | 7                      | 0                                                   |
| 10d             | 0                  | 16                    | 11                     | 7                      | 0                                                   |
| 11              | 8                  | 0                     | 26                     | 0                      | 0                                                   |
| 13              | 5                  | 79                    | 8                      | 3                      | 0                                                   |
| 14              | 10                 | 0                     | 20                     | 10                     | 0                                                   |

In the first stage of screening, we used discriminating concentrations of the test compounds. The compounds 3b, f-h, 5a showed a high insecticidal and miticidal activity. The death rate of *Musca domestica* and *Sitophilus oryzae* was 90–100% (Table 1). The solution of salt 3b and 5a killed 100% of the housefly. The solutions of salts 3f–h killed 90–100% of both
housefly and rice weevil. However, with a decrease in the concentration of compounds to 0.05%, insect death did not exceed 42%.

Compounds 4a, 7a–c, 10b, 13 had a relatively high insecticidal and miticidal activity, resulting in 60–85% death of the tested objects. Other compounds showed no insecticidal activity at all, or their activity was not important.

The nematicidal activity of studied compounds was either very low or completely absent. Only when using salt 3b, the reduction of gall formation on cucumber roots was 73%.

All salts 2a-d, 3a-h, 4a-c, 5a, b, 7a-c, 8, 10a-d, 11, 13, and 14 were tested for bactericidal activity. In this investigation, we used eight objects: four types of fungi, which were tested on solid media (Penicillium cyclopium, Fusarium moniliforme, Aspergillus niger, Venturia Inaequalis); one type of bacteria (Xanthomonas malvacearum); three types of fungi, which exist on green plants, gray rot of the beans (Botrytis cinerea), cucumber powdery mildew (Oidium erysiphoides), the late blight of tomatoes (Phytophthora infestans).

The test results of the salts 2a-d, 3a-h, 4a-c, 5a, b, 7a-c, 8, 10a-d, 11, 13, and 14 are shown in Table 2.

Table 2. The test results of fungicidal activity of compounds 2a-d, 3a-h, 4a-c, 5a, b, 7a-c, 8, 10a-d, 11, 13, 14.

| Compounds number | Colonies of bacteria and fungi, concentration of 0.003% | Concentration of 0.1% | Concentration of 0.05% |
|------------------|--------------------------------------------------------|-----------------------|-----------------------|
|                  | Xanthomonas malvacearum | Fusarium moniliforme | Penicillium cyclopium | Venturia Inaequalis | Aspergillus niger | Phytophthora infestans | Botrytis cinerea | Oidium erysiphoides |
| 2a               | 12 | 18 | 16 | 31 | 22 | 0 | 0 | 0 |
| 2b               | 13 | 18 | 0 | 25 | 12 | 0 | 0 | 0 |
| 2c               | 20 | 5 | 0 | 18 | 0 | 0 | 0 | 0 |
| 2d               | 12 | 24 | 22 | 6 | 22 | 50 | 0 | 43 |
| 3a               | 11 | 7 | 5 | 10 | 0 | 45 | 0 | 17 |
| 3b               | 14 | 11 | 6 | 18 | 20 | 0 | 0 | 0 |
| 3c               | 31 | 20 | 38 | 11 | 5 | 41 | 0 | 19 |
| 3d               | 25 | 24 | 22 | 29 | 0 | 80 | 0 | 0 |
| 3e               | 0 | 14 | 11 | 12 | 0 | 0 | 0 | 0 |
| 3f               | 14 | 19 | 35 | 6 | 12 | 0 | 0 | 0 |
| 3g               | 28 | 29 | 47 | 20 | 0 | 0 | 0 | 0 |
| 3h               | 14 | 12 | 5 | 0 | 0 | 0 | 50 | 0 |
| 4a               | 18 | 9 | 16 | 12 | 5 | 0 | 0 | 0 |
| 4b               | 5 | 6 | 21 | 5 | 0 | 5 | 54 | 50 |
| 4c               | 25 | 27 | 5 | 6 | 11 | 54 | 0 | 0 |
| 5a               | 21 | 17 | 0 | 0 | 6 | 0 | 0 | 0 |
| 5b               | 21 | 29 | 17 | 0 | 5 | 0 | 38 | 0 |
| 7a               | 20 | 27 | 18 | 18 | 18 | 0 | 0 | 58 |
| 7b               | 6 | 21 | 18 | 18 | 6 | 0 | 0 | 28 |
| 7c               | 20 | 5 | 18 | 12 | 0 | 0 | 0 | 22 |
| 8                | 7 | 23 | 35 | 12 | 31 | 0 | 0 | 0 |
| 10a              | 20 | 18 | 6 | 11 | 5 | 0 | 7 | 50 |
| 10b              | 25 | 36 | 33 | 25 | 16 | 0 | 0 | 0 |
| 10c              | 6 | 6 | 11 | 12 | 0 | 0 | 20 | 50 |
| 10d              | 18 | 9 | 22 | 25 | 22 | 0 | 0 | 25 |
| 11               | 43 | 20 | 27 | 11 | 0 | 0 | 0 | 0 |
| 13               | 12 | 27 | 16 | 12 | 16 | 0 | 0 | 0 |
| 14               | 31 | 30 | 33 | 11 | 10 | 56 | 0 | 0 |

Compound 3d showed good activity against the Phytophthora infestans. Inhibition of the growth and development of the Phytophthora infestans was 80%.

The activity of compounds 2d, 3h, 4b, c, 7a, 10a-c, 14 was relatively high. Inhibition of the growth and development of the bacteria and fungi was 50–69% (see Table 2).
We also tested the salts 2a-d, 3a-h, 4a-c, 5a, b, 7a-c, 8, 10a-d, 11, 13, and 14 for herbicidal activity. In the first stage of screening, we studied the activity of these compounds on five test objects: wheat, oats, sorghum, radish, and buckwheat. The concentration of each compound was 5 kg per hectare. The studies were carried out in two ways: spraying the soil before sowing of the seeds and spraying the vegetative part of the plants. Unfortunately, the tested substances had no herbicidal activity.

4. Conclusions

Thus, the alkali metal salts of the quinone mono- and dioxime were synthesized by the reaction of the corresponding quinone oxime with alkali metal hydroxide. Divalent metal salts were obtained in two stages. The first stage was the synthesis of sodium salt of the quinone oxime. The second step was the reaction of the latter with a divalent metal salt. Copper and zinc salts of [(4-oxocyclohexa-2,5-dien-1-ylidene)amino]oxidanide showed the highest insecticidal activity against the house fly and rice weevil. The death index was 90–100%. Copper

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\text{[(2-methyl-4-oxo-5-(propan-2-yl)cyclohexa-2,5-dien-1-ylidene)amino]oxidanide}
\]

showed good activity against the Phytophthora infestans. Inhibition of the growth and development of the Phytophthora infestans was 80%.

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Conflicts of Interest

The authors declare no conflict of interest.

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