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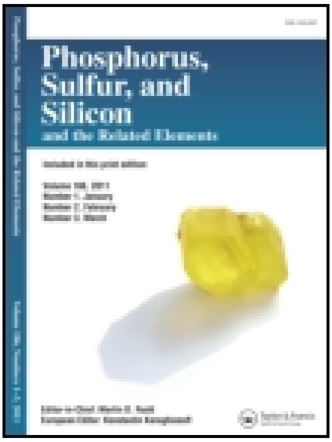

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# Terpene Analogues of Dithiophospate Pesticides

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# TERPENE ANALOGUES OF DITHIOPHOSPATE PESTICIDES

**Rafael A. Cherkasov,[1] Artem V. Sofronov,[1] Yevgeniy M. Martianov,[1] Il'yas S. Nizamov,[1,2] and Dmitriy A. Terenzhev[3]**
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**Abstract** *New optically active O,O-diterpenyl dithiophosphoric and O-terpenyl aryldithiophosphonic acids were prepared when chiral terpenols such as (1R)-endo-(+)-fenchyl alcohol, (1S)-endo-(−)-borneol, (1R)-(−)-nopol, and (1R,2S,3S,5R)-(+)-isopinocampheol were involved in reactions with tetraphosphorus decasulfide and 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides.*

**Keywords** Chiral terpenols; 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides; dithiophosphonic acids; dithiophosphoric acids; optical activity; tetraphosphorus decasulfide

## INTRODUCTION

Common methods of synthesizing dithiophosphate pesticides are usually based on the reactions of the O,O-dialkyl dithiophosphoric acids or their salts with chloroanhydrides of carboxylic acids, esters, and amides of $\alpha$-chlorocarboxylic acids or diethyl maleate. This approach allows traditional dithiophosphate pesticides bearing pharmacophoric functionalities in the S-organyl substituents to be obtained. In contrast to this, we have developed a new approach for synthesizing terpene analogues of dithiophospate pesticides with additional pharmacophoric functionalities in O-organyl group.

## RESULTS AND DISCUSSION

The interest in O-terpenyl derivatives of tetracoordinated phosphorus thioacids is due to their potential metabolic regulation activity. We have used a series of chiral terpenols such as (1*R*)-*endo*-(+)-fenchyl alcohol, (1*S*)-*endo*-(−)-borneol, (1*R*)-(−)-nopol, and (1*R*,2*S*,3*S*,5*R*)-(+)-isopinocampheol. Optically active O,O-diterpenyl dithiophosphoric acids were prepared when (1*S*)-*endo*-(−)-borneol and (1*R*)-*endo*-(+)-fenchyl alcohol were involved in reactions with tetraphosphorus decasulfide at 50°C for 1 h in the benzene suspension. These acids were transformed into the corresponding ammonium salts. The

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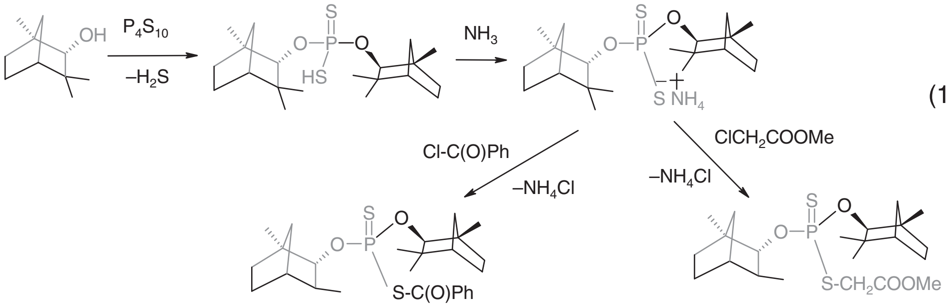
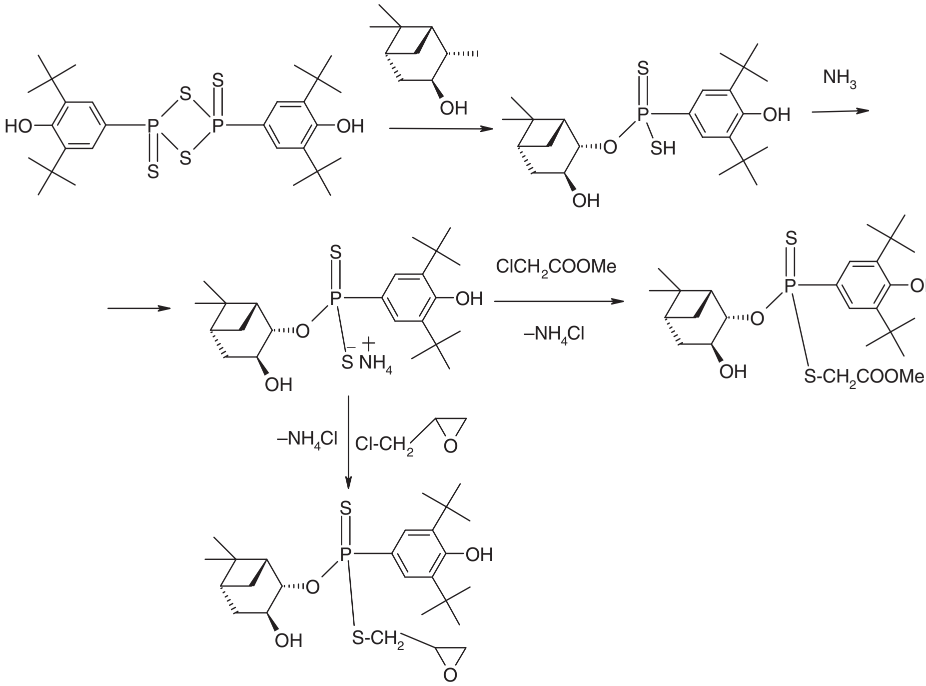
reactions of these salts with benzoyl chloride, methyl chloroacetate, or epichlorohydrin at 20°C for 1 h result in novel S-organyl O,O-diterpenyl dithiophosphates [Eq. (1)].



(1)

Thiophosphorylation of (1*R*)-*endo*-(+)-fenchyl alcohol, (1*S*)-*endo*-(−)-borneol, and (1*R*,2*S*,3*S*,5*R*)-(+)-isopinocampheol by 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides at 50°C for 1 h in the benzene suspension yields new O-terpenyl aryldithiophosphonic acids. Similarly, the corresponding ammonium salts were obtained from these O-terpenyl aryldithiophosphonic acids. These salts were transformed into the pesticide analogues containing the dithiophosphonic units by the reactions with benzoyl chloride, methyl chloroacetate, or epichlorohydrin at 20°C for 1 h [Eq. (2)].



(2)

The S-organyl O,O-diterpenyl dithiophosphates and O-terpenyl aryldithiophosphonates that were prepared possess antimicrobial activity.