tuberactinamine analogs. In addition, all the chemical shifts and coupling patterns of protons in other amino acid residues showed satisfactory similarities to those of tuberactinomycins, especially tuberactinomycin O.

From all the results shown above, it could be now concluded that the structures of capreomycins IA and IB must be revised at least in the amino acid sequences in the cyclic peptide moiety, only remaining a mode of linkage of β-lysine of the branched part undetermined whether to α-amino group of Dpr[2] or to β-amino group of Dpr[4]. In order to establish the decisive whole structure, a total synthesis of capreomycins is now in progress in our laboratory. The results on the synthetic work will be reported elsewhere.

[15] A part was presented at the 13th Symposium on Peptide Chemistry, Tokyo, 1975. Details will be reported soon elsewhere.

[16] The ratio was calculated from the integration of CH_3 protons of alanine on the basis of those of other protons on NMR-spectrum. The value was concomitant to the result of amino acid analysis of the sample.

Phosphorus-Containing Heterocycles as Fungicides: Synthesis of 2,2′-Diphenylene Chlorophosphonate and 2,2′-Diphenylene Chlorothiophosphonate

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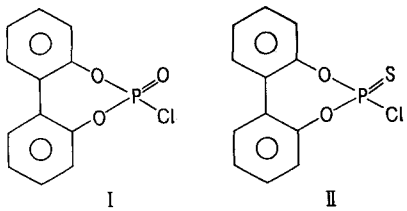
Summary. Synthesis of 2,2′-diphenylene chlorophosphonate and 2,2′-diphenylene chlorothiophosphonate is described through the interaction of 2,2′-dihydroxybiphenyl with phosphoryl chloride and thiophosphoryl chloride respectively. These compounds were screened for their fungicidal activity.

Biphenyl[1] is commonly used as fungicide for citrus fruits. Its 2-hydroxy derivative (Dowicide I)[2] is an important fungicide for the post harvest treatment of citrus fruits to reduce the incidence of rot in stored fruit. Phosphoryl and thiophosphoryl-ester linkages are frequently encountered in organic chemicals used as pesticides[3]. So it would be interesting to synthesize ring systems having phosphoryl/thiophosphoryl-ester moieties fused to biphenyl systems which are expected to increase the biological activity of organic compounds. In the present communication, we wish to report the synthesis of 2,2′-diphenylene chlorophosphonate (I) and 2,2′-diphenylene chlorothiophosphonate (II) and the comparison of their fungicidal activity with that of Dowicide I.

Reaction of phosphoryl chloride on 2,2′-dihydroxybiphenyl in refluxing benzene and in the presence of a base produced (I) in 60% yield, recrystallized from acetone, m.p. 112°. UV-spectrum exhibited λ_{max}^{MeOH} 246 nm (ε 10500). Far IR-spectrum showed strong absorption at 475 and 525 cm^{-1} attributed to P–Cl linkage. IR-spectrum showed usual absorption at 750, 810 (aromatic), 1310 (P = O) and 950, 1235 (P–O–aryl)[4]. Mass spectrum showed molecular ion peak at *m/e* 266. Other fragments were observed at 231 (M^+–Cl), 215 (M^+–Cl–O) and at 199 (M^+–2O–Cl).

Reaction of thiophosphoryl chloride on 2,2′-dihydroxybiphenyl in benzene and in the presence of pyridine gave (II) in 65% yield, recrystallized from acetone, m.p. 105°. UV-spectrum exhibited λ_{max}^{MeOH} 243 nm (ε 16800). IR-spectrum showed absorption at 750, 815 (aromatic), 960, 1240 (P-O-aryl) and 1230 cm^{-1} (P = S). Mass spectrum exhibited prominention peaks at *m/e* 282 (M^+), 266 (M^+–0), 247 (M^+–Cl), 231 (M^+–O–Cl) and 215 (M^+–2O–Cl).



I II

The fungicidal activity of the title compounds was examined against some of the important plant pathogenic fungi. The pure cultures of the organisms were obtained from the department of Plant Pathology, Punjab Agricultural University, Ludhiana and grown on Czapek's (Dox) agar medium at 25° in the presence/absence of the test chemicals[5]. The relative growth of the organisms was then compared (Table)[6].

Fungi	Inhibition (%)[a]		
	Dowicide I (standard; 1000 ppm)	Compound I (1000 ppm)	Compound II (1000 ppm)
Rhizoctonia solani	100	21	19
Fusarium oxysporum	100	17.2	22
Alternaria sp.	100	15	17
Colletotrichum sp.	100	10	7.5
Phytophthora infestans	100	5.8	4.8

[a] As compared to the controls lacking fungicides.

Biphenyl and its 2-hydroxy derivative (Dowicide I) are potent fungicides. When phosphoryl/thiophosphoryl-ester linkage is fused to biphenyl ring system in a cyclic fashion, the fungicidal activity is significantly reduced, which is contrary to the general fact that these moieties, when present in open chains, enhance their fungicidal properties[3].

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[3] M. Kado and E. Yoshinaga, Residue Rev. *25*, 133 (1969).

[4] C. N. R. Rao, *Chemical Application of Infrared Spectroscopy* (Academic Press, New York 1963).

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