SOME LUPININE DIALKYL PHOSPHATE, DIALKYL PHOSPHOROTHIOATE, AND ALKYL ALKYLPHOSPHONOTHIOATE ESTERS

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Lupinine with mp 69° C (petroleum ether) was obtained by saponifying O-acetyllupinine, isolated by the acetic anhydride acetylation of the combined alkaloids of technical anabasine sulfate. The acid chlorides Cl—P(O)$(OCH_3)_2$, Cl—P(O)$(OC_2H_5)_2$, Cl—P(O)(OC_4H_9), Cl—P(S)$(OC_2H_5)_2$, and Cl—P(S)$(OC_2H_5)(CH_3)$ were synthesized by known methods [1–5]. By the reaction of these substances with lupinine, its dialkyl phosphate, dialkyl phosphorothioate, and alkyl alkylphosphonothioate esters were prepared in order to determine their insecticidal activities (table). The analyses of all the compounds corresponded to the calculated figures.

Some Properties of Dialkyl Phosphate, Dialkyl Phosphorothioate, and Alkyl Alkylphosphonothioate Esters of Lupinine

Composition	Developed formula	Yield, %		n_D^{20}, deg	R_f
$C_{12}H_{24}O_4NP$	$C_{10}H_{18}NO(O)P(OCH_3)_2$	68	128 (0,5)	1,4970	0,25
$C_{14}H_{28}O_4NP$	$C_{10}H_{18}NO(O)P(OC_2H_5)_2$	54	134 (0,3)	1,5052	0,31
$C_{18}H_{36}O_4NP$	$C_{10}H_{18}NO(O)P(OC_4H_9)_2$	49	141 (0,3)	1,5114	0,40
$C_{14}H_{28}NO_3PS$	$C_{10}H_{18}NO(S)P(OC_2H_5)_2$	25	152 (0,3)	1,5025	0,21
$C_{13}H_{26}NO_2PS$	$C_{10}H_{18}NO(S)P(OC_2H_5)(CH_3)$	32	148 (0,5)	1,4756	0,29

To 0.04 mole of lupinine in 25 ml of anhydrous ether at −2–0° C was added 0.02 g-mole of the corresponding acid chloride, and the mixture was kept at room temperature for 12 hr. The hydrochlorides were separated off, the filtrate was evaporated, and the reaction products were isolated by preparative thin-layer chromatography on Al_2O_3 (activity grade III, plates 28 × 28 cm) with a 5-mm layer of sorbent, the amount of substance deposited being 1 g, and the solvent being benzene–methanol (300 : 18). The separation was monitored by chromatography in a thin nonfixed layer of Al_2O_3 (plates 20 × 9 cm, spots revealed with iodine vapor). The benzene–methanol (25 : 1.5) system was used for the oxygen derivative and petroleum ether–methanol (25 : 1.5) for the thio derivatives. The IR spectrum (UR-10, KBr) had absorption bands at 1240 cm^{-1} (P=O) and 840 cm^{-1} (P=S).

Thus, the possibility of obtaining dialkyl phosphate, dialkyl phosphorothioate, and alkylphosphonothioate esters of lupinine has been shown. Conditions have been found for their isolation on Al_2O_3 and also for their chromatography in a thin nonfixed layer of Al_2O_3.

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