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### Aminoalkynephosphonic Acids in Agricultural Fungicides: A New Development in Crop Protection Chemicals

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## AMINOALKYNEPHOSPHONIC ACIDS IN AGRICULTURAL FUNGICIDES: A NEW DEVELOPMENT IN CROP PROTECTION CHEMICALS

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Aminophosphonic acids and related derivatives have previously attracted attention as possible plant-growth regulators and for their potential as herbicides. We have now shown that a number of amino-alkanephosphonic acids of the general type  $(\text{HO})_2\text{P}(\text{O})\text{CR}^3\text{R}^4(\text{CH}_2)_n\text{NR}^1\text{R}^2$  have useful fungicidal activity, especially for agricultural use (1). Arising from extensive laboratory tests and field trials  $\alpha$ -amino-propanephosphonic acid (code number PNL 62) has been developed for commercial application under the draft common name ampropylfos. This new pesticide is especially useful primarily as a seed-dressing agent for the control of Drechslera teres. Both R- and S-isomers are active. The compound shows no phytotoxic activity and is of very low mammalian toxicity ( $\text{LD}_{50} > 5000 \text{ mg kg}^{-1}$ ). Within the series of aminophosphonic acids investigated, activity was greatest when the amino group is in the alpha position. Activity decreased with increasing branching in the alkyl chain and was removed by the presence of various substituents (alkyl, tosyl, benzyloxycarbonyl, or trichloromethyloxycarbonyl) on the amino nitrogen.  $\alpha$ -Aminopropanephosphonic acid, which is readily soluble in water, exhibits extensive intermolecular hydrogen-bonding in the solid phase as shown by single crystal X-ray diffraction. <sup>1</sup>H nmr spectroscopy is complicated by the presence of the chiral  $\alpha$ -carbon atom and magnetic non-equivalence of the  $\beta$ -CH<sub>2</sub> protons. Fast-atom bombardment mass spectrometry is particularly useful for identification and gives an intense MH<sup>+</sup> peak with fragmentations involving the loss of HPO<sub>3</sub> or H<sub>3</sub>PO<sub>3</sub> only. Methods for the preparation of  $\alpha$ -aminoalkanephosphonic acids are discussed.

- (1) D. G. Cameron, H. R. Hudson, I. Lagerlund and M. Pianka, Eur. Pat. Appln. EP 153,284, 20 Aug 1985; Chem. Abstr. 1986, 104, 207445k.