

### Synthesis and Configurational Analyses of Chiral Phosphates (1979-84).

In the early days we developed a  $^{31}\text{P}$  NMR method based on quadrupolar effect of  $^{17}\text{O}$ ; this method, along with the isotope effect of  $^{18}\text{O}$ , form the basis for the configurational analysis of chiral phosphates by  $^{31}\text{P}$  NMR. This method has allowed systematic analyses of phosphorus stereochemistry in various enzymatic reactions. Along this line, he has been one of the major players in the field of phosphorus stereochemistry in enzymatic reactions. The work involved extensive organic syntheses of various substrate and product analogs. The most noticeable of these studies is the synthesis and configurational analysis of a chiral analog of inorganic phosphate, [ $^{16}\text{O}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ ]PS.

1. "Use of  $^{31}\text{P}$  Nuclear Magnetic Resonance to Distinguish Bridge and Non-bridge Oxygens of  $^{17}\text{O}$ -enriched Nucleoside Triphosphates. Stereochemistry of Acetate Activation by Acetyl CoA Synthetase," M.-D. Tsai, *Biochemistry* 18, 1468-1472 (1979).
2. "Applicability of the  $^{31}\text{P}(^{17}\text{O})$  NMR Method in the Study of Enzyme Mechanism Involving Phosphorus," M.-D. Tsai, S. L. Huang, J. F. Kozlowski and C. C. Chang, *Biochemistry* 19, 3531-3536 (1980).
3. "Chirality at a Pro-pro-prochiral Phosphorus Center, Stereochemical Course of the 5'-Nucleotidase-Catalyzed Reaction," M.-D. Tsai and T. T. Chang, *J. Am. Chem. Soc.*, 102, 5416-5418 (1980).
4. "Stereochemistry of the Hydrolysis of Adenosine 5'-Thiophosphate Catalyzed by Venom 5'-Nucleotidase," M.-D. Tsai, *Biochemistry* 19, 5310-5316 (1980).
5. "Effects of  $^{17}\text{O}$  and  $^{18}\text{O}$  on  $^{31}\text{P}$  NMR: Further Investigation and Applications," R. D. Sammons, P. A. Frey, K. Bruzik and M.-D. Tsai, *J. Am. Chem. Soc.* 105, 5455-5461 (1983). – This paper was featured in a news article in *Science* 224, 377 (1984).
6. "Stereochemistry of Biological Reactions at Pro-prochiral Centers." H. G. Floss, M.-D. Tsai, and R. W. Woodard, *Topics in Stereochemistry*, E. L. Eliel, N. L. Allinger and S. H. Wilen, Eds., John Wiley & Sons, pp. 253-321 (1984).
7. "Use of Chiral thiophosphates and the Stereochemistry of Enzymatic Phosphoryl Transfer." M.-D. Tsai, in  *$^{31}\text{P}$  NMR: Principles and Applications*, D. Gorenstein. Ed., Academic Press, pp. 175-197 (1984).