**03.4-08** MODEL COMPOUNDS FOR ENZYME-SUBSTRATE INTERACTIONS. By C. P. Huber, P. R. Carey and D. J. Phelps. Division of Biological Sciences, National Research Council of Canada, Ottawa, Canada K1A 0R6.

The enzyme papain forms enzyme-substrate intermediates with various cinnamic acid derivatives, and X-ray diffraction and resonance Raman spectroscopy have been used jointly in studying the mode of interaction. The r. R. spectra of the intermediates are distinctly different from those of the unbound substrates and a group of model compounds has been found which mimics the absorption and r. R. properties of the acyl enzymes and substrates. Crystal structure determinations have been made for 4-dimethylamino-3-nitrocinnamic acid (DMANCA) and 4-dimethylaminocinnamoyl imidazole (DMACI). The former represents the free product and the latter mimics the spectral properties of the bound substrate. By comparison with the DMANCA structure, there is a clear tendency in the DMACI structure toward quinoid character and a small but significant shortening and lengthening of the ethylenic single and double bonds respectively. We believe that a similar highly polarized π-electron system may be occurring in the substrate in the active site by interaction of the acyl residue with protein dipoles and/or hydrogen bonds.

Both compounds crystallize in the monoclinic space group $P2_1/c$ with Z=4. Cell dimensions for DMANCA are a= 18.213(7), b= 7.111 (5), c= 8.736(4) Å, β= 93.88(2)°, and R= 0.044 for 1697 observed reflections. For DMACI a= 8.375(7), b= 6.565(1), c= 23.783(9) Å, β= 101.81(4)° and R= 0.050 for 1861 observed data.

**03.4-09** CRYSTALLOGRAPHIC STUDIES ON THE INTERACTION OF ALKALI AND ALKALINE EARTH METAL SALTS WITH PEPTIDES. By P. Chakrabarti, K. Venkatesan and C. N. R. Rao, Department of Organic Chemistry and Solid State and Structural Chem. Unit, Indian Institute of Science, Bangalore, India.

Binding of alkali and alkaline earth metal salts to peptides and proteins is of great importance to many biophysical phenomena. Unfortunately, little is known about the nature of binding of these salts to the peptide bond. We have, therefore, chosen N- methylacetamide as a model peptide and prepared its complexes with LiCl, $NaClO_4$, KSCN, $MgCl_2$, $CaCl_2$ and carried out systematic X-ray structure analyses of these crystalline complexes. The binding of the metal changes the peptide geometry considerably and a regularity has been found in the approach of the metal cations to the carbonyl group.

**03.4-10** THE STRUCTURE AND ABSOLUTE CONFIGURATION OF THREE AJUGAREPTANSONES. By C. Miravitlles and X. Solans, Instituto "Jaime Almera", C.S.I.C., Egipciacas 15, Barcelona-1, Spain. G. Germain and J.P. Declercq, Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, 1 Place Louis Pasteur, B-1348, Louvain-la-Neuve, Belgium.

The description of the isolation and chemistry of the three natural closely related compounds, Ajugareptansin-p-Bromobenzoate (I), Ajugareptansone A(II) and Ajugareptansone B(III), is made by Camps, Coll, Cortel and Messeguer(1979) (Tetrahedron Lett, 19, 1709-1712)and Camps, Coll and Cortel (1981) (Tetrahedron Lett, in press). These compounds exhibit an insect antifeedant activity and are diterpenoids with a clerodane skeleton. The structure (I and II) was solved using the MULTAN system of computer programs (Main, Woolfson, Lessinger, Germain and Declercq, 1978), and the structure (III) was solved using the Patterson search system (Braun, Hornstra and Leenhouts. Philips Res Repts.,(1969), 24, 85-118). The refinements of the three structures were made using the SHELX program system (Sheldrick,(1976) SHELX). The absolute configuration was determined (I, II) by the Bijvoet difference method and is the same as that of other clerodane compounds, Clorodendrin A p-bromobenzoate chlorhydrin (Kato, Munkata, Katayama, J.Chem.Soc. Perkin.

II, (1973), 69-73) 3-epicaryoptin and Clerodin (Rogers, Unal, Williams, Ley, Sim, Joshi and Ravindranath, J.Chem.Soc. (1979), 97-99).

Crystal Data

| | I | II | III |
|---|---|---|---|
| | $C_{36}H_{47}BrO_{11}$ | $C_{29}H_{40}O_{10}$ | $C_{24}H_{29}O_8$ |
| | 733.7 | 548.6 | 445.5 |
| | monoclinic | orthorhombic | orthorhombic |
| | $P2_1$ | $P2_12_12_1$ | $P2_12_12_1$ |
| a | 14.152(5)Å | 16.225(3)Å | 10.681(8)Å |
| b | 15.662(4)Å | 11.007(3)Å | 9.758(7)Å |
| c | 8.182(2)Å | 16.401(3)Å | 21.320(13)Å |
| β | 93.31(3)° | ---- | ---- |
| Z | 2 | 4 | 4 |
| V | 1810(1)$A^3$ | 2929(1)$A^3$ | 2222(3)$A^3$ |
| Dc | 1.35 $Mgm^{-3}$ | 1.24 $Mgm^{-3}$ | 1.34 $Mgm^{-3}$ |