

variable jet separator to a Varian MAT CH5D mass spectrometer. Spectra were processed and recorded by a Varian 620/L computer.

Results and discussion. α -Multistriatin and α -cubebene were identified in the extract of female-infested elm volatiles by comparison of their mass spectral fragmentation patterns with those of authentic specimens (figure) and by accurate mass measurement of the molecular ions. 4-Methyl-3-heptanol (which shows no molecular ion) was identified in the same extract from its mass spectral fragmentation pattern (figure). These assignments were confirmed by co-injections of the Porapak Q extract with authentic samples on both the capillary GC columns. GC and GC-MS examination of the extract of *U. procera* volatiles showed that of the above 3 compounds only α -cubebene was present.

Although the components of the aggregation pheromone produced by *S. multistriatus* on *U. americana* are also

produced by *S. scolytus* virgin females on *U. procera* it is not yet known what part they play in the aggregation behaviour of *S. scolytus*. Multilure does not appear to attract *S. scolytus* in large numbers in the field⁹. Further work on the components of the secondary attraction in *S. scolytus* is now in progress.

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Further information on the mechanism of the cystathionine- γ -synthase catalyzed reactions from the assignment of the $^1\text{H-NMR}$ spectrum of homoserine

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Summary. Unambiguous assignment of the $^1\text{H-NMR}$ resonances due to the hydrogen atoms in the β -position of homoserine indicates that the hydrogen which is exchanged and removed in the cystathionine- γ -synthase catalyzed reactions holds the pro-R configuration.

The knowledge of the absolute configuration of the hydrogen atom in the β -position of L-homoserine which is stereospecifically exchanged and removed in the conversion of O-succinylhomoserine into cystathionine or, in the absence of cysteine, into α -ketobutyrate by cystathionine- γ -synthase from *Salmonella typhimurium*¹ has been thought to be useful for a proper mechanistic interpretation of the isotopic studies² carried on with this pyridoxal phosphate dependent enzyme.

We have unambiguously assigned the $^1\text{H-NMR}$ signals relative to the β -hydrogen atoms of homoserine using stereospecifically deuteriated materials³, and found that the upfield absorbing β -proton, which has been reported² to be exchanged and removed in the cystathionine- γ -synthase catalyzed reactions, holds the pro-R configuration. This means that in the methylene interconversion occurring in the enzymic transformation of O-succinylhomoserine into α -ketobutyrate, protonation of the intermediate leading to the latter compound takes place from the same side from which the hydrogen had been removed in the homoserine-coenzyme intermediate Schiff's bases. The retention of configuration therefore supports, most economically, the previous idea schematized in the reported reaction path⁴ that a single polyhydric base is present on the enzyme active side to remove both the α and the β pro-R hydrogen atoms in the formation of the enzyme-bonded vinylglycine derivative. The latter picks up a proton into the γ -methylene group from the same protonated base in the tautomerization to the (Z)-aminocrotonate derivative⁵, as shown from the intramolecular hydrogen transfer from the α and β to the γ position of the C_4 framework. The latter intermediate is protonated in the β -position from the identical reprotonated base to

give, eventually, after hydrolysis, α -ketobutyrate with overall retention of configuration in the β -methylene group.

This picture would be in line with the results of studies on the mechanism of pyridoxal phosphate dependent enzymes⁶, and with recent views on the general significance of the enzyme reaction stereospecificity⁷. The assignment of the $^1\text{H-NMR}$ resonances due to the β -methylene group of homoserine obtained by stereoselective deuteration is in agreement with that recently reported based on instrumental methods⁸.

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