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4-Methyleneproline : Synthetic Studies

RECENTLY, Gray and Fowden¹ have reported the isolation of a new amino-acid, 4-methylene proline (I), from seeds of loquat (*Eriobotrya japonica*). Structure (I) was firmly established by both chemical and spectroscopic evidence; but during the course of another investigation we have confirmed it by synthesis. This synthesis serves also to clarify some ambiguity concerning the optical configuration of the new amino-acid.

Wittig reaction² between benzyloxycarbonyl-4-oxo-L-proline (II)³ and methylenetriphenylphosphorane (III) yielded the oily benzyloxycarbonyl derivative of 4-methylene-L-proline. Its crystalline dicyclohexylamine salt had m.p. 160–161° [α]_D¹⁹ – 5.5° (c. 2 in chloroform) (found: C, 70.89; H, 8.63; N, 6.53. C₂₆H₃₅O₄N₂ requires C, 70.55; H, 8.65; N, 6.33 per cent). The natural amino-acid, generously provided by Dr. L. Fowden, was converted into its benzyloxycarbonyl derivative by treatment with benzylchloroformate at pH 10.3 (autotitrator) in aqueous acetone; the dicyclohexylamine salt had m.p. 139° and no detectable optical rotation in chloroform solution (found: C, 70.21; H, 8.48; N, 6.63 per cent). In the solid state (nujol mulls) the two salts had distinctly different infra-red spectra, although the absorption bands corresponding to the principal functional groups were similar. In chloroform solution, however, the spectra were identical. Evidently the natural amino-acid is racemic, and this was confirmed by hydrogenation to a mixture of the *cis*- and *trans*-4-methylprolines (mainly the *cis* isomer⁴). We have shown previously that the optical rotations of the *cis* and *trans* isomers of 4-methyl-L-proline are both large and negative (–85° and –57° respectively)⁴. However, the hydrogenation product of the natural 4-methyleneproline had, within the limits of experimental error, no detectable rotation, and it can be concluded that less than 1 per cent of optically active material can be present.

4-Methyleneproline isolated from loquat seeds is therefore racemic, as suspected by Gray and Fowden¹. This result is surprising, both in view of the rare occurrence of racemic amino-acids in Nature, and since the most plausible biogenetic precursor, 4-methylene-glutamic acid, has already been isolated in an optically active form⁵, although from a different plant source.

Benzyloxycarbonyl-4-methylene-L-proline is a possible precursor for stereospecific synthesis of 4-hydroxymethylproline, the configuration of which is at present a matter of discussion⁷.

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Use of Amines in Inorganic Hydrolysis

FOLLOWING the work of Smith and Page¹, amines have been widely used for the extraction of acids from aqueous solutions. We have applied this process to the hydrolysis of inorganic salts in aqueous solution without the introduction of any reagents into the aqueous phase. An amine which is immiscible with the aqueous phase is used to extract the acid formed on the hydrolysis of the salt and under suitable conditions insoluble complexes can be precipitated. Thus complexes of UO₂⁺⁺, Th⁴⁺, Fe³⁺ and RuNO³⁺ have been precipitated by us, and although the anion has usually been nitrate we have also carried out precipitations from sulphate media. Other anions could also be used since amines extract many acids efficiently (see, for example, Moore²).

The hydrolysis of uranyl nitrate can be made to proceed until a uranium complex is precipitated; for example, in a typical experiment when a 0.89 M solution of uranyl nitrate in water was stirred with 0.5 M trinonylamine (tri-3 : 5 : 5-trimethylhexylamine) in xylene for 5 min. at room temperature a yellow precipitate was formed. After washing with water and drying at 60° C. the composition of the solid corresponded to UO₃·2H₂O (found: U = 73.2 per cent, H₂O = 12.7 per cent; calculated for UO₃·2H₂O, U = 73.8 per cent, H₂O = 11.2 per cent). The product was contaminated by xylene as shown by a carbon content of 0.76 per cent; but nitrogen could not be detected showing that no amine was present. The identity of the product was confirmed by X-ray examination and by differential thermal analysis (which indicated that it was the α -form of UO₃·2H₂O).

The precipitated complexes are probably of the type UO₃·2H₂O·x amine and their stability varies with the type of amine, for example, with a tertiary amine, such as trinonylamine, the amine can be removed by thorough washing followed by drying at 60° C., but this is not the case if a primary amine such as 'Primene JM-T' (a proprietary mixture of alkyl primary amines with carbon chains ranging