A New Naturally-occurring Nitro-compound

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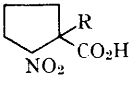
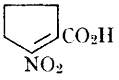
WHEN *Aspergillus wentii* is grown on liquid media it produces broths which cause unusual morphological changes in higher plants.[1] We have shown the active principle to be 1-amino-2-nitrocyclopentanecarboxylic acid (I; R = NH_2)[2] and report below some of its properties.

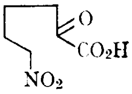
Hydrolysis of the amino-acid (I; R = NH_2) [$\nu_{max.}$ 3530, 3350, 2570, 2040, 1675, 1620, 1570, and 1525 cm.$^{-1}$; nuclear magnetic resonance spectrum (in trifluoroacetic acid): triplet (1H) (J = 9 c./sec.) at τ 4·46, multiplet (6H) at τ 7–8] with boiling water leads, with loss of ammonia, to a mixture containing 1-hydroxy-2-nitrocyclopentanecarboxylic acid (I; R = OH) as major component and 2-nitrocyclopent-1-enecarboxylic acid (II). We have shown that these hydrolysis products are in equilibrium under the conditions of formation and that the unsaturated acid (II) is the first to be formed.



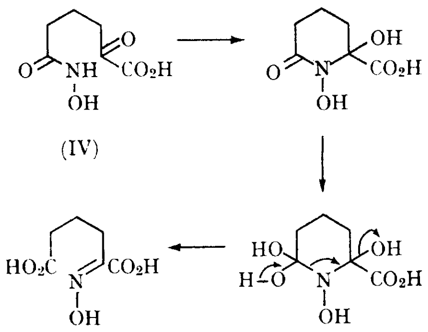
(I)



(II)



(III)



(IV)

(V)

Hydrolysis of the amino-acid (I; R = NH_2) or of the hydroxy-acid (I; R = OH) with hot mineral acid yields glutaric acid, carbon dioxide, and ammonia. An explanation of this somewhat surprising result was suggested by the observation that treatment of the hydroxy-acid (I; R = OH) with concentrated sulphuric acid at 80° yields α-oximinoadipic acid. If this compound is an intermediate in the acid hydrolysis then the

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[1] P. W. Brian, G. W. Elson, H. G. Hemming, and M. E. Radley, *Nature*, in the press.
[2] B.P. appln. No. 47001/62.

products are explained by the fact that α-oximinocarboxylic acids readily decompose to cyanides with one carbon atom less.[3] The key to the formation of α-oximinoadipic acid, and to other reactions in this series, is the opening, by reverse aldol-type reaction, of the cyclopentane ring to give the open-chain compound (III). Since it is known[4] that primary nitro-compounds are converted into hydroxamic acids by mineral acid we have only to postulate a "trans-hydroxylamination" (*e.g.* IV → V) to explain the formation of α-oximinoadipic acid.

The structure of the amino-acid (I; $R = NH_2$) has been confirmed by its synthesis[5] *via* the iodo-compound (I; $R = I$) formed by treatment of cyclopent-1-enecarboxylic acid with dinitrogen tetroxide in the presence of iodine (*cf.* ref. 6). The iodo-compound is converted into the amino-compound with ammonia and to the unsaturated compound (II) with pyridine, a by-product of the latter reaction being cyclopent-1-enecarboxylic acid.

It is of interest that *A. wentii* produces β-nitropropionic acid as well as 1-amino-2-nitrocyclopentanecarboxylic acid. Since β-nitropropionic acid has been shown[7] to be derivable from aspartic acid but not from β-alanine it seemed likely that 1-amino-2-nitrocyclopentanecarboxylic acid arises from αε-diaminopimelic acid rather than from lysine. In fact we find that diaminopimelic acid is not incorporated, and that lysine is specifically incorporated, into 1-amino-2-nitrocyclopentanecarboxylic acid.

The amino-acid (I; $R = NH_2$) is optically inactive either as a result of racemisation during the isolation procedure, which involves contact with aqueous ammonia, or because its biosynthesis involves non-enzymatic stages.

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[3] W. Dieckmann, *Ber.*, 1900, **33**, 579.
[4] Cf. *e.g.* S. B. Lippincott and H. B. Hass, *Ind. Eng. Chem.*, 1939, **31**, 118.
[5] B.P. appln. No. 16500/64.
[6] T. E. Stevens and W. D. Emmons, *J. Amer. Chem. Soc.*, 1958, **80**, 338.
[7] A. J. Birch, B. J. McLoughlin, H. Smith, and J. Winter, *Chem. and Ind.*, 1960, 840.