



sis<sup>5</sup> of an identical product starting from dehydrodiconiferyl alcohol,<sup>6</sup> the substance is assigned structure II. Further work to confirm this structure is in progress.

From the brown-coloured, probably oligomeric and polymeric acidolysis products which were accumulated in fraction C, no individual products have been isolated so far.

The relation of the degradation products mentioned above to specific lignin structures will be discussed in forthcoming detailed publications.

In gel filtration of aqueous solutions of aromatic compounds, the "molecular sieving" action of the gel (Sephadex) was found<sup>7</sup> to be obscured by adsorption effects. It was therefore surprising to find that fractionation in the order of molecular size had taken place in the experiments reported above.

Gel filtration experiments<sup>8</sup> with mixtures of lignin model compounds (monomeric models such as ketol I, 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone and vanillin, as well as dimeric models such as pinoresinol and dehydrodiconiferyl alcohol), showed that adsorption effects were greatly suppressed if mixtures of water and certain polar organic solvents (e.g. dioxane) were used as eluants.

It is intended to apply the combination of gel filtration and chromatographic separation methods to lignin degraded in different ways. An investigation of lignin degradation products obtained under the conditions of kraft and soda cooking is presently being carried out.

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## Ozonolysis of Acetylenedicarboxylic Acid

E. BERNATEK, T. LEDAAL and S. ÅSEN

*Universitetets Kjemiske Institutt,  
Blindern, Oslo 3, Norway*

Ozonolyses in formic acid with the formation of performic acid have been reported.<sup>1,2</sup> Investigations on this reaction have recently been extended to maleic acid and its anhydride.<sup>3,4</sup>

Acetylenedicarboxylic acid, dissolved in concentrated formic acid, did not absorb ozone quantitatively, and a large excess of the reagent had therefore to be applied in order to ensure a complete reaction. The reaction mixture contained active oxygen, but performic acid could not be detected by direct titration nor by distillation *in vacuo*. After evaporation of the solvent, the reaction product was a mixture of crystals. About one fourth of it was oxalic acid and the remainder an acid  $C_2H_4O_6$ . This acid was dibasic and contained one atom of active oxygen. It could be reduced to tartronic acid and dehydrated to mesoxalic acid. The evidence should prove the new acid to be hydroperoxymaleonic acid (I).



Acetylenedicarboxylic acid (0.50 g) in a mixture of glacial acetic acid (40 ml) and acetic anhydride (10 ml) was ozonized for 90 min at 10°C. The solvent was removed *in vacuo* and the oily residue crystallised only with difficulty. Recryst. four times from nitromethane it had m.p. 130°. (Found: C 37.9; H 3.8; act. O 7.3. Calc. for  $C_7H_8O_8$ : C 38.2; H 3.6; act. O 7.3). Titrated rapidly in the cold: E = 74.7. If alkali was added in excess and retitrated E = 57.0. Calc. for  $C_7H_8O_8$ : E tribasic 73.3, E tetrabasic 55.0.  $C_7H_8O_8$  (59.5 mg) was refluxed in water for 10 h. The reaction mixture smelled somewhat of acetic acid. After removing the solvent, the residue was dried over potassium hydroxide (37.5 mg, calc. 36.8 mg). It contained active oxygen and had m.p. 120°C, which was undepressed in mixture with hydroperoxymalonic acid.

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## On the Structure of the New Amino Acid A, 2-Methylenecycloheptene-1,3-diglycine, Isolated from the Mushroom

### *Lactarius helvus*

ERKKI HONKANEN, TAUNO MOISIO,  
ARTTURI I. VIRTANEN

Laboratory of the Foundation for Chemical Research, Biochemical Institute,  
Helsinki, Finland

and ATTILIO MELERA

Varian A.G., Research Laboratory,  
Zürich, Switzerland

In an earlier paper by Casimir and Virtanen<sup>1</sup> the occurrence of four new amino acids (A, B, C, and D) in the mushroom

*Lactarius helvus* was described. All these amino acids give on the paper chromatogram with ninhydrin characteristic yellow or yellow-brown spots which after a while turn violet. Komamine and Virtanen,<sup>2</sup> using the method of Linko,<sup>3</sup> showed that the amino acid A contained two  $\alpha$ -amino and  $\alpha$ -carboxyl groups. On catalytic hydrogenation two moles of hydrogen, or on bromination two moles of bromine, were consumed per mole of the amino acid, showing the presence of two double bonds. The double bonds were not conjugated. Elemental analysis of the compound A gave an empirical formula of  $C_{11}H_{18}N_2O_4$ .<sup>2</sup>

In continued investigations with a larger amount of material it was observed that the so-called amino acid A was a mixture of three, perhaps isomeric compounds ( $A_1$ ,  $A_2$ , and  $A_3$ ). By crystallization of this mixture several times from water, the amino acid  $A_1$  most difficultly soluble in cold water was obtained in pure form. Its IR-spectrum showed it to be identical with the amino acid A prepared by Komamine and Virtanen.<sup>2</sup> On catalytic hydrogenation, amino acid  $A_1$  gave two dihydrogenation products, indicating that a new asymmetric carbon atom was formed in the molecule and that the carbon chain must be branched at the position of the double bond. The NMR spectrum of the amino acid  $A_1$  showed that it contained no methyl group. Two ring olefinic and two terminal olefinic protons were, however, evident. After catalytic hydrogenation a well defined signal of a secondary methyl

group  $H-\overset{|}{C}-CH_3$  was found. The amino

acid  $A_1$  must therefore contain a  $>C=CH_2$  group, from which the new asymmetric carbon atom is formed on hydrogenation.

By oxidation of the amino acid  $A_1$  with ninhydrin followed by steam distillation only traces of a volatile compound were obtained. The mass spectrum of this compound was typical of a dialdehyde having a molecular weight of 164, indicating the formula  $C_{10}H_{12}O_2$  for this dialdehyde. Its 2,4-dinitrophenyl-hydrazone showed an absorption maximum at 355  $m\mu$ , which is characteristic of aldehydes having no  $\alpha,\beta$ -double bonds. Therefore the double bonds in the dialdehyde molecule are not conjugated with the carbonyl groups.

By ninhydrin oxidation of the hydrogenated amino acid the corresponding saturated dialdehyde (mol. wt. 168,  $C_{10}H_{16}O_2$ )