sis ⁵ of an identical product starting from dehydrodiconiferyl alcohol, ⁶ 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 7 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 ⁸ 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

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

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

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 C₃H₄O₆. 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 hydroperoxymalonic acid (I).

The hydroperoxide group is fairly stable and is difficult to detect with ordinary reagents, which probably is due to a strong hydrogen bonding.

Ozonolysis must evidently in this case have occurred with the loss of one carbon atom, but without total cleavage of the triple bond. The mechanism of this reaction has so far not been studied in detail, but we should like to propose a possible pathway:

Acetylenedicarboxylic acid is strong enough to be partly ionised (II) and the primary ozone complex (III) is thought to break down in the manner indicated, giving the ketene intermediate (IV). The step from (III) to (IV) is analogous to one proposed by Dobinson 5 in the ozonolysis of the sodium salt of phenanthrene-9-carboxylic acid in aqueous solution, where phenanthrenequinone was the main product. Formic acid will add rapidly to the ketene giving the anhydride (V). This can be hydrolysed by the small amounts of water present, or the water may add directly to the ketene. (V) can probably also be converted to (I) by loss of carbon monoxide. The possibility of a direct attack of the solvent on the intermediate (III) can of course not be excluded.

If the ozonolysis of acetylenedicarboxylic acid had followed the usual pattern for acetylenes, one could have expected

the formation of some diketosuccinic acid. This compound has never been found in our reaction mixtures.

In glacial acetic acid the ozonolysis evidently took a similar course as in formic acid, hydroperoxymalonic acid again being the main product. On the other hand, if the acetic acid was mixed with 25% acetic anhydride, another peroxy compound was formed from the ozonolysis. It had the composition $C_7H_8O_8$, contained one atom of active oxygen and could, depending on the conditions, be titrated as a tribasic or tetrabasic acid. The substance could be hydrolysed to hydroperoxymalonic acid (I) and is considered as having the structure (VI), which has been formed by addition of acetic acid to the ketene (IV), and by acetylation of the hydroperoxide group by acetic anhydride, or by attack of the mentioned reagents on the intermediate (III).

Experimental. Acetylenedicarboxylic acid (5.00 g) in formic acid (50 ml, 98-100 %) was treated with ozonised oxygen (4.9 % wt.) for 5 h at a flow rate of 30 l/h. The mixture was evaporated in vacuo and the residue dried over potassium hydroxide. It consisted of two types of crystals which were separated mechanically. The larger crystals were identified as oxalic acid, while, the remainder contained active oxygen. Recryst. from nitromethane, m.p. 120° . (Found: C 26.4; H 2.9; act. O 11.7; E 68.2. Calc. for $C_3H_4O_6$ dibasic: C 26.5, H 2.9, act. O 11.8, E 68.0). $C_3H_4O_6$ (0.510 g) was hydrogenated catalytically (Pt/ BaSO₄, 2%). The residue (0.455 g; calc. 0.450 g) had m.p. 158°, undepressed on mixture with authenic tartronic acid. (Found: C 29.3; H 3.4; E 64.1. Calc. for C₃H₄O₅ dibasic: C 30.0; H 3.3; E 64.5). The identity with tartronic acid was also proven by its infra-red spectrum. $C_3H_4O_6$ (0.26 g) was dissolved in anhydrous isopropyl ether (20 ml) to which anhydrous zinc chloride (0.3 g) was added. The mixture was heated gently until the active oxygen had disappeared (45 min) and extracted with water. A p-nitrophenylhydrazone was prepared from the extract. M.p. 202°C. The literature 6 gives for mesoxalic acid p-nitrophenylhydrazone 202°C. (Found: C 42.7; H 2.8; N 16.5. Calc. for C₉H₇N₃O₄ C 42.7; H 2.8; N 16.6).

Acetylenedicarboxylic acid (0.50 g) in a mixture of glacial acetic acid (40 ml) and acetic anhydride (10 ml) was ozonised 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,H,O,: 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. $\dot{C}_7 \dot{H}_8 \ddot{O}_8$ (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,

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In an earlier paper by Casimir and Virta-nen 1 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, 2 using the method of Linko,3 showed that the amino acid A contained two a-amino and acarboxylgroups. 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 $C_{11}H_{18}N_{2}O_{4}$.²
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 (A1, A2, and A3). By crystallization of this mixture several times from water, the amino acid A₁ most difficultly soluble in cold water was obtained in pure from. Its IR-spectrum showed it to be identical with the amino acid A prepared by Komamine and Virtanen.² On catalytic hydrogenation, amino acid A₁ 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 A₁ 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-C-CH₃ was found. The amino

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

By oxidation of the amino acid A1 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 C₁₀H₁₂O₂ for this dialde-Its 2,4-dinitrophenyl-hydrazone showed an absorption maximum at $355 \text{ m}\mu$, which is characteristic of aldehydes having no α,β -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, H, O,)

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