ture could demonstrate that even slight modifications in the formula of DDT almost generally result in the complete or at least very substantial loss of the efficacy; however, a kind of "dimerization" of DDT as expressed in the structure of II does not lead to such a deactivation. Moreover, the efficiency of II (mol. wt., 638.08) renders a trifle questionable Riemschneider's[3] assumption that ≃430 should be the upper limit for the m. wt. of insecticidally active compounds.

[3] Riemschneider, *Seifensieder Ztg.*, **73**, *Chem.-techn. Fabrikant*, **43**, 73 (1947); *C. A.*, **43**, 345c (1949).

DEPARTMENT OF PHARMACEUTICAL CHEMISTRY
UNIVERSITY OF LIEGE (BELGIUM) J. BERNIMOLIN

RECEIVED APRIL 29, 1949

PRODUCTS FROM THE DEGRADATION OF LIGNIN BY SODIUM HYDROSULFIDE

Sir:

We wish to report the isolation and partial identification of a series of degradation products of lignin which have been obtained as a result of a reaction described by one of us several years ago.[1] When wood was treated with aqueous solutions of carefully prepared pure sodium hydrosulfide at temperatures in the neighborhood of 180°, relatively high yields of ether-soluble oils were found among the reaction products. The purity of the sodium hydrosulfide was found to be a controlling factor in the formation of these degradation products.

We have since that time succeeded in isolating many of the components of these ether-soluble oils by solvent fractionation and by fractional distillation. Our general procedure has been as follows: Extractive free aspen wood was heated for two hours in an autoclave at 180° with an excess of a 7% aqueous solution of sodium hydrosulfide. The reaction mixture was acidified with hydrochloric acid and exhaustively extracted with *n*-butanol. The butanol extract, after concentration, was dispersed into petroleum ether to remove interfering amorphous products as an insoluble residue. The soluble products were further separated by extraction with aqueous sodium bicarbonate and sodium hydroxide into neutral, phenolic, and acidic fractions amounting, respectively, to 4.3, 3.9 and 5.4 of the original oven-dry wood. These fractions represent a yield of 90% based on the Klason lignin. In the extraction with sodium hydroxide, small amounts of sodium hydrosulfite were added to prevent serious oxidation of the catechols which were found to be present.

Each of these fractions was then further divided by extraction with ligroin into a soluble low boiling and an insoluble high boiling fraction to facilitate the subsequent fractional distillation. The various products were given a simple vacuum distillation prior to the fractional distillation.

Among the constituents of the phenolic fraction, we have identified the following compounds: *Phenol:* aryloxyacetic acid m. p. 98–99°, authentic m. p. 98–99°, mixed m. p. 98–99°; 3,5-dinitrobenzoate m. p. 144–144.5°, authentic m. p. 144°, mixed m. p. 144°. *o-Cresol:* aryloxyacetic acid m. p. 147–149°, authentic m. p. 152–153°, mixed m. p. 151–152°. *Pyrocatechol:* m. p. 104–105°, authentic m. p. 104–105°, mixed m. p. 104–105°; 3,5-dinitrobenzoate m. p. 157–157.5°, authentic m. p. 159–159.5°, mixed m. p. 157–159.5°. *Acetovanillone:* m. p. 112.5–114°, authentic m. p. 112.5–114°, mixed m. p. 113–114°; 2,4-dinitrophenylhydrazone m. p. 237–237.5°, authentic m. p. 238.5–239.5°, mixed m. p. 237–237.5°; semicarbazone m. p. 168–168.5°, authentic m. p. 168–169°, mixed m. p. 167.5–168.5°. 2,6-Dimethoxyphenol: 3,5-dinitrobenzoate m. p. 166.5–167.5°, authentic m. p. 165.5–167°, mixed m. p. 165–167°, —OCH_3 calcd. for $C_{15}H_{12}O_8N_2$, 17.82; found 18.10.

This report is to the writers' knowledge the first instance in which phenol and *o*-cresol have been isolated as products of degradation of wood or lignin by a process other than one of pyrolysis. In order to eliminate the possibility that these compounds had arisen as a result of pyrolytic cleavage in the distillation of the original crude phenolic fraction, they were again isolated by a second independent method. A portion of the crude phenolic fraction was steam distilled and the distillate containing the phenol and cresol fractionally distilled under reduced pressure. At no time was the material subjected to a temperature exceeding 140° as measured in the oil-bath. This work will be published in full later.

DIVISION OF FORESTRY AND DAVID L. BRINK
DIVISION OF AGRICULTURAL BIOCHEMISTRY
UNIVERSITY OF MINNESOTA RALPH L. HOSSFELD
ST. PAUL, MINN. W. M. SANDSTROM

RECEIVED APRIL 28, 1949

[1] Hossfeld, Gortner and Kaufert, *Ind. Eng. Chem.*, **35**, 717 (1943).

SEPARATION OF MONONUCLEOTIDES BY ANION-EXCHANGE CHROMATOGRAPHY

Sir:

As part of a study of the metabolism of nucleic acid, methods have been developed for the quantitative separation and isolation of the several ribose mononucleotides from their mixtures. These separations, of considerable interest to those concerned with the analysis, isolation and preparation of nucleotides, make use of the established principles of ion-exchange,[1] successfully applied to difficult inorganic separations in this laboratory.[2]

Although fair separations by cation-exchange are feasible,[3] anion-exchange offers several practical advantages among which are freedom from hydrolysis, wide choice of eluting agents with respect to replacing anion and *p*H, and ease of recovery and concentration. The latter two of

[1] Reviewed by Tompkins, *J. Chem. Educ.*, **26**, 32, 92 (1949).

[2] Tompkins, Khym and Cohn, THIS JOURNAL, **69**, 2769 (1947).

[3] Cohn, *Science*, **109**, 377 (1949).

these have already made possible the separation of a new isomer of adenylic acid[4] (see Fig. 1).

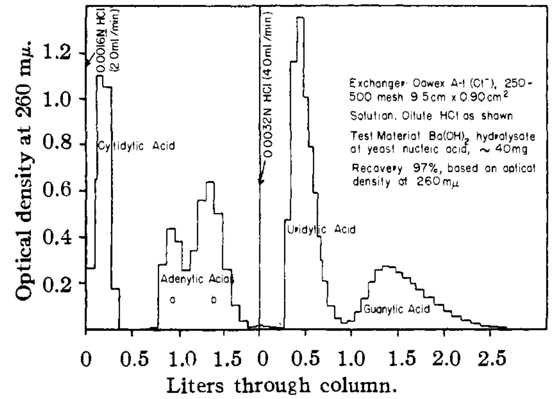

Fig. 1.—Separation of mixed monoribonucleotides by anion-exchange.

The type of separation possible is completely illustrated in Fig. 1. The mixture was adsorbed on the strong-base anion-exchanger from a small volume of an essentially neutral and salt-free solution, although larger volumes or salt-containing solutions can be adsorbed at higher *p*H's, and eluted with dilute hydrochloric acid. Similar separations have been achieved with acetic and formic acids while less satisfactory separations can be made at higher *p*H's. Bases and ribosides do not interfere and may be individually separated at higher *p*H values.[3] Concentration and recovery of the separated components is easily achieved by addition of base, readsorption on 10-fold smaller columns and elution with stronger acid or salt solutions. Crystalline material has been prepared in this manner, the rate of crystallization being slower than the rate of elution from the column. Thus it is possible to recover pure crystalline compounds from complex mixtures by ion-exchange alone.

(4) Carter and Cohn, *Federation Proceedings*, **8**, 190 (1949).

BIOLOGY DIVISION
OAK RIDGE NATIONAL LAB.
OAK RIDGE, TENN. WALDO E. COHN

RECEIVED APRIL 18, 1949

ON THE DEGRADATION OF COLLAGEN INTO A "PARENT GELATIN"[1]

Sir:

Scatchard, *et al.*,[2] have postulated that collagen on hydrolysis yields an undegraded "parent" gelatin molecule of dimensions 800 Å. by 17 Å. This communication compares these results with these obtained by direct observation of the formation of gelatin from intact collagen in solution.

The outflow times[3] at 20° of ichthyocol solutions[4] treated for varying lengths of time at two different temperatures are presented in the Figure. Evidently, ichthyocol degrades rapidly into a product which degrades further at a slower rate.

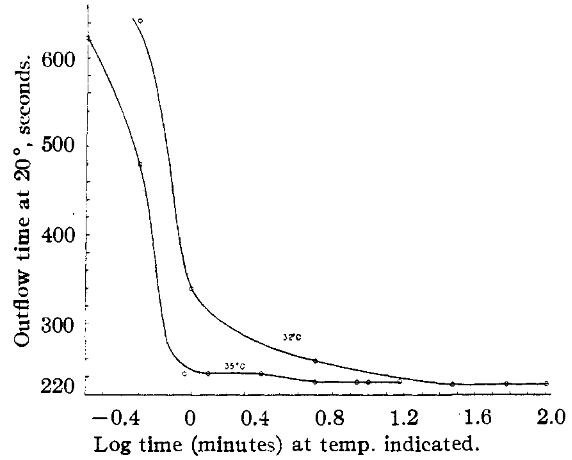

Fig. 1.—Solvent outflow time at 20°, 209.3 seconds; *p*H 2.5; 0.2 *M* NaCl.

The viscosity increment[5] of the solution which showed no further rapid change was approximately 160, which, with Simha's[6] equation, yields an axial ratio of 47.5. Assuming that the diameters of the gelatin molecule in this case and in that of Scatchard, *et al.*, are the same, the length of the parent gelatin molecule is about 800 Å.

The heat of activation[7] for the process of formation of the parent gelatin in the presence of salt is of the order of 20–30 kcal. per mole, while the further degradation of the parent gelatin has a heat of activation of about 10 kcal. per mole.[8] The heats of activation are without much meaning except to indicate differences in order of magnitude.

DEPARTMENT OF BIOLOGY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS TORSTI P. SALO[9]

RECEIVED MARCH 30, 1949

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(1) This paper represents a partial report on research sponsored by the office of the Quartermaster General, Research and Development Branch, under Project No. 130-46 on "Determination of the Nature and Properties of Skin Structure" under direction of the Leather Subcommittee of the National Research Council Committee on Quartermaster Problems."

(2) Scatchard, Oncley, Williams and Brown, THIS JOURNAL, **66**, 1980 (1944).

(3) Measured with an Ostwald-Fenske type capillary viscosimeter at 20°.

(4) Tunic of carp swim-bladder was extracted with 0.05% acetic acid in the cold and was filtered under suction successively through Number 41 H Whatman paper, coarse and medium sintered glass filters. The filtrate, dialyzed exhaustively in the cold against an acetic acid solution of *p*H 2.5 and 0.2 *M* with respect to sodium chloride, was diluted with the latter solution to an ichthyocol concentration of 0.11%.

(5) The relative viscosities of dilutions of the parent gelatin solution with respect to the *p*H 2.5 0.2 *M* sodium chloride solution were determined and used to calculate the viscosity increment, assuming a partial specific volume of 0.75 for gelatin.

(6) Simha, *J. Phys. Chem.*, **44**, 25 (1940).

(7) Assuming equal outflow times at 20° mean equal amounts degraded.

(8) Degradation at 60 and 80°. Outflow times measured at 20°.

(9) Department of Chemistry, University of Tennessee, Knoxville, Tennessee.