

TABLE I  
HEXADECYL SULFIDES

Sulfides	Tri-	Tetra-	
M. p., °C.	41.2-41.9	35.9-36.5	
Yield, %	62	67	
Formula	C <sub>32</sub> H <sub>66</sub> S <sub>3</sub>	C <sub>32</sub> H <sub>66</sub> S <sub>4</sub>	
Sulfur, %	Calcd.	17.58	22.15
	Found	17.10 17.35	21.78 21.71
X-Ray		13.0	11.9
	dif-	4.39 <sup>b</sup>	5.14
frac-		4.26	4.66 <sup>a</sup>
	tion,	4.03	3.82
Å.		3.82 <sup>a</sup>	3.70 <sup>b</sup>
		3.70	3.58
		3.32	

<sup>a</sup> Most intense line. <sup>b</sup> Second most intense line.

**Hexadecyl Trisulfide.**—A solution of 0.5 mole of sulfur dichloride in 150 ml. of petroleum ether was added slowly to a stirred solution of 1 mole of hexadecyl mercaptan in 500 ml. of petroleum ether, the temperature rising from 17 to 27°. After all of the sulfur dichloride had been added, the reaction mixture was refluxed for one hour to drive off hydrogen chloride. The solution was then diluted with an equal volume of dry acetone, chilled and the resulting white crystals recrystallized from a mixture of equal volumes of petroleum ether and acetone.

**Hexadecyl Tetrasulfide.**—The same procedure as above was followed, except that 0.25 mole of sulfur monochloride and 0.5 mole of hexadecyl mercaptan in 250 ml. of petroleum ether was used. Also, the final crystals were further purified by twice dissolving in petroleum ether and acetone and cooling.

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RECEIVED NOVEMBER 27, 1946

## COMMUNICATIONS TO THE EDITOR

### HIGHLY POLYMERIZED DESOXYPENTOSE NUCLEIC ACID FROM YEAST

Sirs:

The isolation of highly polymerized desoxy-pentose nucleic acid (DNA) from yeast is described below.

A chilled suspension of fresh washed baker's yeast (800 g.) in 0.1 *M* sodium citrate (180 cc.) was passed through a bacterial mill<sup>1</sup> (placed at our disposal through the courtesy of Dr. D. E. Green). On centrifugation at 4000 r. p. m. for ninety minutes two solid layers sedimented, the lower one consisting of intact cells. The upper layer (290 g.), containing, among other cellular fragments, material stainable by the Feulgen technique, was treated with one volume of 1 *M* sodium chloride solution.<sup>2</sup> The addition of 2 volumes of alcohol to the supernatant resulting from the centrifugation of the very viscous mixture for 120 minutes at 4000 r. p. m. produced threads which were easily separated from a granular precipitate. (All operations were performed in the cold.)

The threads were dissolved in 1 *M* sodium chloride solution (300 cc.) and freed of protein by repeated shaking with chloroform-octanol.<sup>3</sup> The amount of extracted DNA, estimated by means of the diphenylamine reaction<sup>4</sup> (standardized against DNA from thymus), corresponded to about 0.04% of the cell debris.

The preparations still contained considerable

(1) V. H. Booth and D. E. Green, *Biochem. J.*, **32**, 855 (1938).

(2) F. Miescher in F. Hoppe-Seyler, "Medicinisch-chemische Untersuchungen," Berlin, 441 (1871).

(3) M. G. Sevag, *Biochem. Z.*, **273**, 419 (1934).

(4) Z. Dische, *Mikrochemie*, **8**, 4 (1930).

amounts of ribonucleic acid and of a hexose-containing polysaccharide which could be removed by electrophoretic fractionation or, more economically, by the following method. The threads produced from the deproteinized solution by 2 volumes of alcohol were dissolved in a 10% calcium chloride solution to give an approximately 0.2% solution. The cloudy viscous solution was clarified by centrifugation at 20,000 r. p. m. and the nucleic acid precipitated as threads with 0.3 volume of alcohol. (The yields were increased by reworking the granular sediments produced in these operations.) To the solution of the combined threads in 0.1 *M* borate buffer of pH 7.8 a small amount (1% of the nucleic acid weight) of crystalline ribonuclease, obtained through the kindness of Dr. M. Kunitz, was added and the mixture subjected to dialysis against the same buffer for fourteen hours at room temperature and then against ice-cold distilled water for one day. The solution was deproteinized once more and evaporated in the frozen state in a vacuum. In this manner around 70% of the DNA present in the original extract was recovered.

The purified preparations were readily soluble in water giving clear highly viscous solutions. Different samples were found to contain 87 to 91% of DNA, 6 to 8% of ribonucleic acid and 3 to 5% of a polysaccharide. A representative specimen contained N 13.5, P 8.3% (N:P ratio 3.6).

The DNA of yeast exhibited an absorption maximum at 2605 Å., a minimum at 2320 Å. Its electrophoretic mobility (phosphate buffer, pH 7.4) was  $-15.7 \times 10^{-5}$ . The specific viscosity of a 0.115% solution in water at 30.3° was 5.9,

the diffusion constant  $D_{20}$   $1.09 \times 10^{-7}$ , corresponding to an axial ratio of about 390.

This work, which will later be reported in detail, has been supported by a research grant from the U. S. Public Health Service.

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RECEIVED MARCH 17, 1947

### THE SYNTHESIS OF CYCLOÏCTATETRAENE FROM PSEUDOPELLETIERINE

Sir:

Validity of the synthesis of cycloïctatetraene from the pomegranate bark alkaloid pseudopelletierine by Willstätter, Waser and Heidelberger<sup>1</sup> has been questioned because their product resembled styrene in some physical and chemical properties,<sup>2</sup> and on the basis of studies of model compounds.<sup>3</sup> The synthesis has not been repeated, presumably because pseudopelletierine was not available. Development of a catalytic synthesis of cycloïctatetraene from acetylene in Germany<sup>4</sup> has renewed interest in the hydrocarbon.

We have repeated the Willstätter synthesis of cycloïctatetraene, beginning with synthetic pseudopelletierine,<sup>5</sup> through the following steps. Pseudopelletierine  $\rightarrow$  N-methylgranatoline (82%)  $\rightarrow$  N-methylgranatenine (85%)  $\rightarrow$  methiodide (97%)  $\rightarrow$   $\alpha$ -des-dimethylgranatenine (I) (82%)  $\rightarrow$  methiodide (92%)  $\rightarrow$  cycloïctatriene (II) (70%)  $\rightarrow$  dibromide (not isolated)  $\rightarrow$  bis-(dimethylamino)-cycloïctadiene (III) (47%)  $\rightarrow$  di-methiodide (97.5%)  $\rightarrow$  cycloïctatetraene (7-9%). Physical constants of the intermediates corresponded closely to those reported originally.<sup>1</sup> Ultraviolet absorption spectra were consistent with conjugated diene structures for I and III, and a conjugated triene structure for II ( $\lambda_{\max}$  2650 Å.,  $\log \epsilon$  3.57).

The cycloïctatetraene which was obtained gave a satisfactory analysis (calcd. for  $C_8H_8$ : C, 92.26; H, 7.74. Found: C, 92.47; H, 7.91), and had the following properties: m. p. (capillary)  $-5.8$  to  $-5.4^\circ$ ;  $n_D^{25}$  1.5342; m. p. (hot stage) of the

(1) Willstätter and Waser, *Ber.*, **44**, 3423 (1911); Willstätter and Heidelberger, *ibid.*, **46**, 517 (1913).

(2) Noted by Vincent, Thompson and Smith, *J. Org. Chem.*, **3**, 603 (1939). Also, dehydrogenation of cycloïctene yields styrene; Goldwasser and Taylor, *THIS JOURNAL*, **61**, 1260 (1939).

(3) Hurd and Drake, *ibid.*, **61**, 1943 (1939). Investigation of other models led to a different conclusion; Hurd and Ensor, paper presented before the Division of Organic Chemistry at the Chicago Meeting of the American Chemical Society, September, 1946 (Abstracts, page 24M). For a review see Baker, *J. Chem. Soc.*, 258 (1945).

(4) Reported in "German Synthetic Fiber Developments," p. 631 (translation of an article by W. J. Reppe), Textile Research Institute, New York, N. Y., 1946 (PB. 7416) and other Department of Commerce reports.

(5) Prepared by modifications of the small-scale synthesis of Schöpf and Lehmann, *Ann.*, **518**, 1 (1935).

(6) Ref. 1 reports m. p.  $-27^\circ$ . Other physical properties are in fair agreement.

maleic anhydride adduct  $166.7-168.2^\circ$ ; per cent. hydrogen absorbed in catalytic hydrogenation over platinum 101.5%. The m. p. of the cycloïctatetraene and its maleic anhydride adduct were not depressed by mixture with a sample prepared from acetylene and its corresponding derivative, respectively. Cycloïctatetraene from the two sources had identical ultraviolet absorption spectra, and showed no important differences in infrared absorption spectra.<sup>7</sup>

(7) We are indebted to Dr. R. C. Lord, Jr., and Mr. R. S. McDonald for the infrared data.

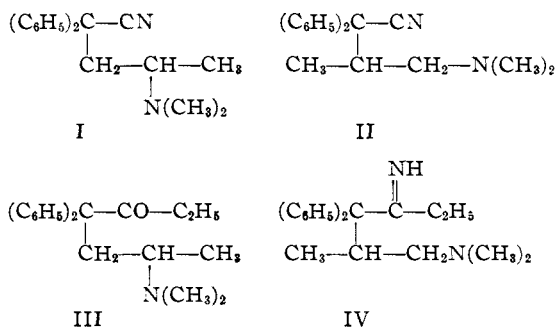
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RECEIVED MARCH 18, 1947

### SOME ISOMERS OF AMIDONE AND RELATED COMPOUNDS

Sir:

It has recently been shown that the reaction between diphenylacetonitrile and 1-dimethylamino-2-chloropropane results in a mixture from which two isomeric aminonitriles (I and II) have been isolated.<sup>1</sup> The higher melting nitrile (I) reacts with ethylmagnesium bromide to yield Amidone (III). We have now found that the lower melting nitrile (II) reacts with ethylmagnesium bromide to give a ketimine (IV) which was isolated as the sesquioxalate (m. p.  $145-146^\circ$ . *Anal.* Calcd. for  $2C_{21}H_{28}N_2 \cdot 3H_2C_2O_4$ : C, 64.99; H, 7.05; N, 6.32;  $H_2C_2O_4$ , 30.45. Found: C, 65.15; H, 6.96; N, 6.36;  $H_2C_2O_4$ , 30.50). This was also characterized as the dihydrochloride (m. p.  $200-202^\circ$  dec. *Anal.* Calcd. for  $C_{21}H_{28}N_2 \cdot 2HCl$ : C, 66.13; H, 7.93; N, 7.35; Cl, 18.59. Found: C, 66.00; H, 7.75; N, 7.30; Cl, 18.43) and the dipicrate (m. p.  $140-141^\circ$ . *Anal.* Calcd. for  $C_{21}H_{28}N_2 \cdot 2C_6H_5O_7N_3$ : C, 51.69; H, 4.47; N, 14.62. Found: C 51.65, 51.75; H, 4.54, 4.38; N, 14.41, 14.58).



This ketimine was found to be remarkably resistant to hydrolysis, being only partially converted to the ketone (Isoamidone II, V) by boiling for five hours with an excess of 20% hydrochloric

(1) E. M. Schultz, C. M. Robb and J. M. Sprague, *THIS JOURNAL*, **69**, 188 (1947).