TABLE I

POLYMETHYLENEDIAMINES

	R	B. p., °C. 1 mm.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
$H_2N(CH_2)_6NR_2$	n-C_3H_7	97–99	72.00	72.28	14.00	14.36	...	...
	n-C_5H_{11}	137–138	75.00	75.03	14.06	14.35	...	...
$H_2N(CH_2)_8NR_2$	n-C_3H_7	109–111	73.68	73.40	14.03	14.27	...	...
	n-C_4H_9	131–132	...	...	...	...	10.83	10.62
	n-C_5H_{11}	148–149	...	...	...	...	9.85	10.18
$H_2N(CH_2)_{10}NR_2$	n-C_3H_7	136–137	75.00	74.93	14.06	14.25	...	...
	n-C_4H_9	142–144	76.05	76.30	14.08	14.51	9.85	9.62

sium phthalimide by the conventional procedures.[6,7] Hydrolysis of these compounds by hydrazine hydrate[8] was more satisfactory than hydrolysis by concentrated hydrochloric acid.

The diamines are listed in Table I. They are colorless, viscous liquids, insoluble in water. They are hygroscopic and absorb carbon dioxide from the air. Efforts to prepare the usual solid derivatives yielded oils which would not crystallize. The hydrochlorides were too hygroscopic to be of value as derivatives.

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(6) Muller and Kraus, *Monatsh.*, **61**, 219 (1932).

(7) Gabriel, *Ber.*, **22**, 1137 (1889).

(8) Ing and Manske, *J. Chem. Soc.*, 2350 (1926).

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RECEIVED MARCH 14, 1945

Bis-(β-alkoxyethyl) Diselenides

Bis-(β-methoxyethyl) Diselenide.—A mixture of 28 g. of potassium sulfite and 9.5 g. of selenium in 300 ml. of 50% ethanol was digested under reflux for an hour. Four grams of anhydrous potassium carbonate and 11.3 ml. of methyl 2-bromoethyl ether in 12 ml. of ethanol were successively added and the refluxing was continued for two more hours. The mixture was acidified with excess 1 *N* hydrochloric acid and then oxidized with 70 ml. of 3% hydrogen peroxide, added slowly with stirring. The diselenide separated out as an orange red oil with a strong alliaceous odor. The oil was washed with warm water, centrifuged and fractionated under reduced pressure; b. p. *124–126° (7 mm.), yield 10 g.*

Properties.—Bis-(β-methoxyethyl) diselenide is a yellow, vesicant oil with alliaceous odor; i, H_2O, s. organic solvents.

Bis-(β-ethoxyethyl) diselenide and bis-(β-butoxyethyl) diselenide also have been prepared. Both are yellow oils of unpleasant odor and are skin irritants.

DATA ON BIS-(β-ALKOXYETHYL) DISELENIDES

Formula			$C_6H_{14}O_2Se_2$	$C_8H_{18}O_2Se_2$	$C_{12}H_{26}O_2Se_2$
Analyses, %	Carbon	Calcd.	26.08	31.57	39.99
		Found	26.23	31.43	40.10
	Hydrogen	Calcd.	5.11	5.97	7.28
		Found	5.29	5.89	7.39
Boiling point	°C.		124–126	135–137	175–177
	Mm.		7	6	6
$d^{25}{}_4$			1.596	1.451	1.303
$n^{25}{}_D$			1.5554	1.5340	1.5150

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RECEIVED FEBRUARY 5, 1945

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COMMUNICATIONS TO THE EDITOR

ORIENTED FIBERS OF SODIUM PECTATE

Sir:

Although brief mention has been made in several places concerning X-ray diffraction investigations of pectin or pectin derivatives, interpretation of the data obtained has not been attempted. This lack of information concerning the structure of this important natural polymer is partly due to the difficulty of getting X-ray diffraction photographs with sufficient reflections to enable a structural analysis to be made.

A short time ago it was noticed from X-ray powder photographs that sodium pectate is highly crystalline. Attempts were immediately made to produce sodium pectate fibers having molecular orientation. Best results were obtained by first making a pectic acid fiber and then converting it to the sodium salt. The pectic acid used was prepared in this Laboratory by the method of Baier and Wilson[1] and had an intrinsic viscosity of 3.8.

A successful method for making well-oriented sodium pectate fibers consisted of titrating a 1% solution of pectic acid to a *p*H of 5.0 with sodium hydroxide. The resulting solution was then forced through a 1-mm. nozzle into a coagulating bath consisting of 85% ethyl alcohol in 1 *N* hydrochloric acid. The resulting wet fiber was strong enough to be handled readily. The hydrated fiber was held in a 60% alcoholic, 0.1 *N* sodium hydroxide solution overnight and then immersed for twenty-four hours in 60% ethyl alcohol. The fiber was then removed and slowly elongated 38% while drying. The dry fiber was strong, pliable, showed good molecular orientation, and was remarkably crystalline (Fig. 1).

The layer line spacings on the X-ray photograph can be measured readily. From these

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(1) W. B. Baier and C. W. Wilson, *Ind. Eng. Chem.*, **33**, 287 (1941).

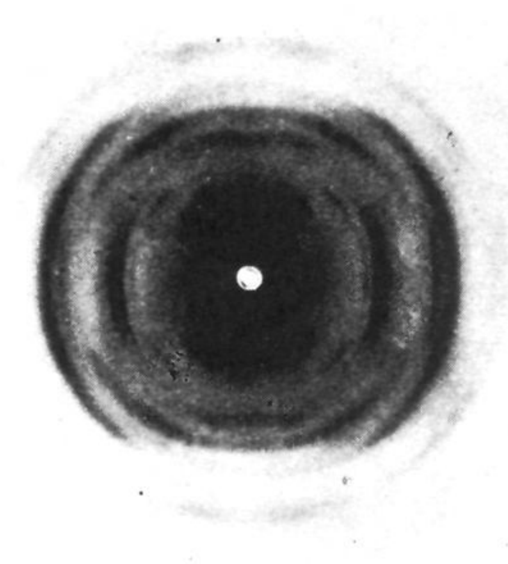

Fig. 1.—X-Ray diffraction photograph of a sodium pectate fiber: CuKα radiation; fiber axis vertical; camera distance 5.0 cm.

values the identity period in the fiber direction can be determined to be approximately 13.1 Å. This value lies between the maximum value (10.4 Å.), observed when there are two pyranose rings in the identity period, as in cellulose and chitin, and the value (15.2 Å.) observed for certain cellulose derivatives[2] when there are three pyranose rings in the identity period.

The symmetry of the galacturonide chain in pectin evidently approximates that of a threefold screw axis but with the angle between the plane of the pyranose rings and the fiber axis somewhat larger than occurs in cellulose and its derivatives. The threefold screw axis is also suggested by the fact that the sodium pectate fiber diagram can be indexed on a hexagonal lattice. The true unit cell can only be pseudohexagonal, however, for reasons that will be discussed elsewhere.

A detailed analysis of the fiber diagram will be published in the near future.

(2) J. Gunderman, *Z. physik. Chem.*, **37B**, 387 (1937).

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ALBANY 6, CALIFORNIA H. LOTZKAR

RECEIVED APRIL 16, 1945

THE SYNTHESIS OF 3,4-DIAMINOCARBETHOXYFURAN

Sir:

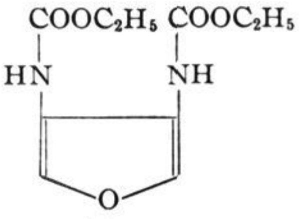
The recent interest in 3,4-diaminocarbethoxyfurans[1] prompts us to record a synthesis of the parent compound of this series (I).

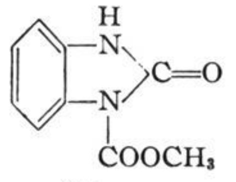
Furan-3,4-dicarboxylic acid was prepared according to the literature.[2] Treatment of the diacid with phosphorus pentachloride in benzene readily gave the diacid chloride in 85% yield. This crystallized from benzene in colorless needles (m. p. 76°; calcd. for $C_6H_2O_3Cl_2$: Cl, 36.7. Found: Cl, 36.5). Hydrolysis of this acid chloride gave a diacid which did not depress the melting point of authentic furan-3,4-dicarboxylic acid. Heating with methyl alcohol gave a dimethyl ester identical with that prepared from the diacid and diazomethane.

Concentrated ammonium hydroxide immediately gave the corresponding diamide (m. p. 262° [dec.]; calcd. for $C_6H_6O_3N_2$: N, 18.18. Found: N, 18.30). It is interesting to note that the success of this method of preparation of the 3,4-diamide is in striking contrast to the great difficulty experienced in attempting to make some similar compounds from the dicarboxylic esters.[3,4]

Reaction of the diacid chloride with sodium azide in cold aqueous acetone gave the corresponding diazide in almost quantitative yield. This compound is stable when moist, but explodes on rubbing when dry. Heating the diazide with ethyl alcohol gave the desired 3,4-diaminocarbethoxyfuran (I) in good yield. It formed small, colorless crystals from ligroin, m. p. 166–167° (calcd. for $C_{16}H_{14}O_5N_2$: N, 11.6. Found: N, 11.4).[5]

It is of interest that the corresponding reaction in the benzene series gives not the diaminocarbethoxy compound, but (II), the cyclized benzimidazole derivative.[6] This is another example of the difficulty of fusing a five-membered ring in the 3,4-position of a furan nucleus.


(I)


(II)

The work reported in this Communication had to be discontinued almost two years ago.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN GILBERT STORK

RECEIVED APRIL 12, 1945

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(1) Hofmann, THIS JOURNAL, **67**, 694 (1945).

(2) Reichstein, Grüssner, Schindler and Hardmeier, *Helv. Chim. Acta*, **16**, 276 (1933).

(3) Seka, *Ber.*, **57**, 1864 (1924).

(4) Bilton and Linstead, *J. Chem. Soc.*, 922 (1937).

(5) Analysis kindly performed by Paul Kletzke.

(6) Lindemann and Schultheis, *Ann.*, **464**, 237 (1928)