***n*-Paraffin Hydrocarbons.**—From the neutral fraction after saponification a waxy product was isolated which, after a thirty-minute treatment in concentrated sulfuric acid at 120°, was crystallized from a mixture (1:1) of Skellysolve B and 95% ethanol. Its physical properties and long spacing (d_{001}) are shown in Table II under total hydrocarbons. A combustion analysis of this sample shows C, 85.11%, H, 14.91%. This indicates a paraffin hydrocarbon, but the limits of error of the analysis do not permit a distinction between $C_{31}H_{64}$ and $C_{33}H_{68}$ or mixtures corresponding to this range of composition. Accordingly, the product was fractionally crystallized by cooling after another sulfuric acid treatment (in which no darkening was observed). Three fractions were obtained. They are shown as fractions 1, 2, and 3 in Table II in the order of increasing solubility in the Skellysolve B–ethanol solution, and hence shorter chain length. The best photographs of the paraffins were obtained with filtered Cu radiation, using a 10-mil collimating system and a sample-to-film distance of 10 cm.

TABLE II

PHYSICAL PROPERTIES OF HYDROCARBON MIXTURES

Sample	First transition point, heating, °C.	M. p., °C.	F. p., °C.	Crystal spacing d_{001}, Å.
Total hydrocarbons	61.7	68.3–68.8	68.3	43.0
Fraction 1	61.9–62.5	68.8–69.4	68.6	43.1
80% C_{31} + 20% C_{33}[a]	62.0	68.8	..	42.8
Fraction 2	61.0–61.6	67.9–68.5	68.3	42.2
95% C_{31} + 5% C_{33}[a]	62.0–62.2	67.9–68.0	67.4	42.0
90% C_{31} + 5% C_{33} + 5% C_{29}[a]	61.0	67.8	..	About 42.0
Fraction 3	59.7–60.0	67.0–67.5	67.0	41.4
80% C_{31} + 20% C_{29}[a]	60.0–60.5	66.6–66.8	66.0	41.5
$C_{31}H_{64}$[b]	62.0–62.5	67.6–67.8	67.3	41.55

[a] A. C. Chibnall, S. H. Piper, A. Pollard, E. F. Williams and P. N. Sahai, *Biochem. J.*, **28**, 2189 (1934). [b] S. H. Piper, A. C. Chibnall, S. J. Hopkins, A. Pollard, J. A. B. Smith and E. F. Williams, *ibid.*, **25**, 2072 (1931).

Chibnall, *et al.*,[7] examined the cuticle constituents of a large number of plants and found that all paraffins present contained an odd number of carbon atoms. We assume this to be true for the paraffins of cryptostegia leaf wax and accordingly have compared our data with those given by Piper[8] and Chibnall[7] for the odd-paraffin hydrocarbons.

The data for fraction 1 agree fairly well with the data for a mixture of 80% $C_{31}H_{64}$ and 20% $C_{33}H_{68}$. The crystal spacing 43.1 Å. is slightly larger than that (42.8 Å.) given by the mixture, indicating that the content of $C_{33}H_{68}$ in this fraction is somewhat greater than 20%.

The melting point and crystal spacing of fraction 2 are in fair agreement with those of a mixture containing 95% $C_{31}H_{64}$ and 5% $C_{33}H_{68}$, but the low transition point of this fraction indicates the presence of a small percentage of $C_{29}H_{60}$. Chibnall[7] lists data for a mixture of 90% $C_{31}H_{64}$, 5% $C_{33}H_{68}$, and 5% $C_{29}H_{60}$, and in fair accord with the data for fraction 2.

The data for fraction 3 are consistent with those for a mixture of about 80% $C_{31}H_{64}$ and 20% $C_{29}H_{60}$. The melting point and crystal spacing of a 50–50 mixture of $C_{33}H_{68}$ and $C_{29}H_{60}$ would be close to the values observed for this fraction, but binary mixtures of paraffins differing in chain length by four or more carbon atoms crystallize in two phases,[8] each phase giving a separate d_{001} value. However, only one phase was observed in each of the fractions.

Acknowledgment.—Acknowledgment is made of the coöperation of C. L. Ogg, who made the microanalyses.

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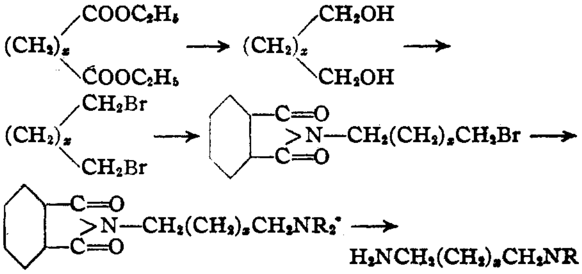
[7] A. C. Chibnall, S. H. Piper, A. Pollard, E. F. Williams and P. N. Sahai, *Biochem. J.*, **28**, 2189 (1934).

[8] S. H. Piper, A. C. Chibnall, S. J. Hopkins, A. Pollard, J. A. B. Smith and E. F. Williams, *Biochem. J.*, **25**, 2072 (1931).

NEW COMPOUNDS

Some Polymethylenediamines[1,2]

Incidental to another problem, a series of diamines of the general formula $H_2N(CH_2)_xNR_2$ has been prepared by the following reactions:



Ethyl adipate, ethyl sebacate and ethyl suberate were reduced to the corresponding polymethylene glycols either with sodium and *n*-butyl alcohol[3] or by catalytic reduction with copper chromium oxide.[4] Yields by both methods were 80–85%.

The polymethylene dibromides were prepared from the glycols by the action of dry hydrogen bromide.[5]

The 1-dialkylaminopolymethylene phthalimides were prepared from the polymethylene dibromides and potas-

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[1] The work described in this paper was done under a contract recommended by the Committee on Medical Research between the Office of Scientific Research and Development and the University of Missouri.

[2] Microanalyses by Lois May and Frances Marx, Microchemical Laboratory, Columbia University.

[3] "Organic Syntheses," Coll. Vol. II, p. 154 (1943).

[4] Ref. 3, p. 325.

[5] "Organic Syntheses," Vol. 20, p. 20.

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).

H. E. FRENCH
CHEMISTRY LABORATORY H. E. UNGNADE
UNIVERSITY OF MISSOURI J. E. POE
COLUMBIA, MISSOURI L. H. EILERS

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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

CHEMICAL LABORATORY
CATHOLIC UNIVERSITY OF AMERICA H. P. WARD
WASHINGTON, D. C. I. LEO O'DONNELL[1]

RECEIVED FEBRUARY 5, 1945

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[1] Present address, St. Mary's College, Winona, Minnesota.

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