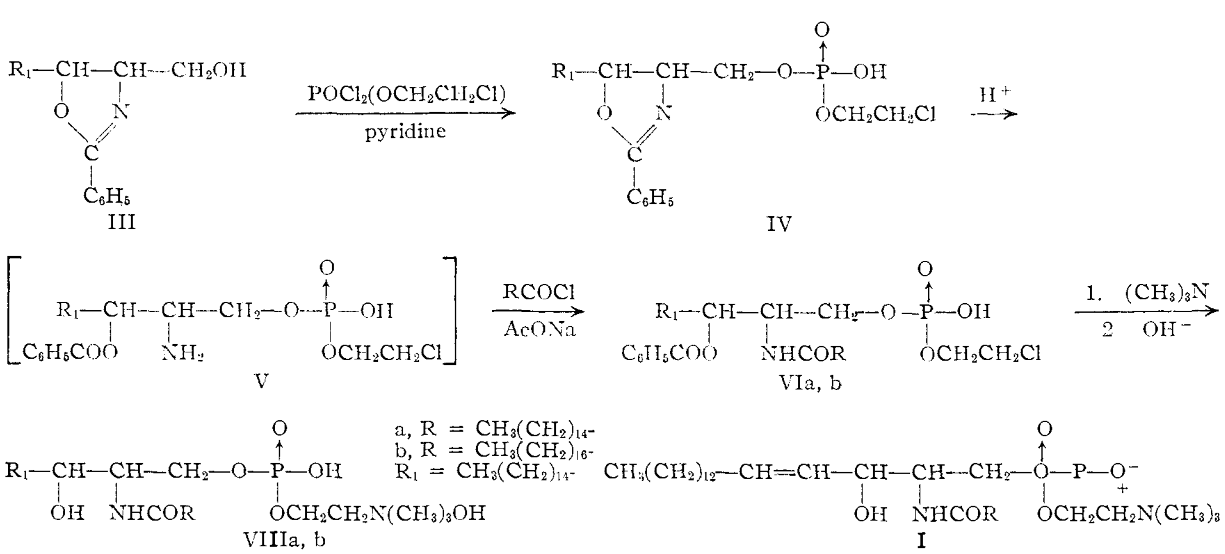

a, R = $CH_3(CH_2)_{14}$-
b, R = $CH_3(CH_2)_{16}$-
$R_1 = CH_3(CH_2)_{14}$-

yield. (Found: C, 53.95; H, 7.41; N, 2.58; Cl, 6.07; P, 5.1; Ba, 11.6.)

Refluxing with the equivalent amount of hydrochloric acid opened the oxazoline ring to give the *erythro* form of the benzoxy ester V which was not isolated, but was acylated with the corresponding acid chlorides in the presence of sodium acetate. Palmitoyl chloride yielded the amide VIa, m.p. 98–99.5°. (Found: C, 65.75; H, 9.8; N, 1.93; P, 3.6; Cl, 4.58.) Prolonged treatment of the barium salt of VIa with trimethylamine[5,6] gave N - palmitoyl - 3 - O - benzoxydihydrosphingosinephosphorylcholine chloride (VIIa), m.p. 170–175°. (Found: C, 65.39; H, 10.43; N, 3.14; P, 3.77.) Removal of the benzoxy group by mild alkaline hydrolysis afforded palmitoyldihydrosphingomyelin (VIIIa), a hygroscopic compound of m.p. 210–212°. (Found: C, 64.1; H, 12.0; N, 3.83; P, 4.17).

Similarly we prepared stearoyl-dihydrosphingomyelin (VIIIb), m.p. 213–214°. (Found: C, 65.97; H, 12.05; N, 3.89; P, 4.18).

The intermediate compounds were characterized as follows: N-steroyl-3-O-benzoxydihydrosphingosinephosphoryl ethylene chlorohydrin (VIb), m.p. 95–97°. (Found: C, 66.38; H, 10.45; N, 1.82; P, 4.04; Cl, 4.01.) N-stearoyl-3-O-benzoxydihydrosphingosinephosphoryl choline chloride (VIIb), m.p. 170–172°. (Found: N, 3.35; P, 3.77.)

Both dihydrosphingomyelins gave analytical carbon values which correspond closely to the hydrated form of the zwitterionic structure I, and are, therefore, expressed by formula VIII. This result is consistent with the behaviour of the lecithins, recently reported by Baer and co-workers.[7]

The infrared spectra of VIIIa and VIIIb (Nujol) were essentially identical and showed characteristic bands at: 2.94, 3.12, 6.1, 6.41, 6.73, 6.95, 8.13, 9.08, 9.43, 10.28, 10.77, 11.41, 12.02, and 13.94 μ. The absorption peaks reported[8] for the natural product are: 3.10, 6.06, 6.42, 6.75, 7.05, 8.12, 9.18, 9.44, 10.29, 10.86, 11.41, 12.01, 13.09 and 13.86 μ.

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THE INCORPORATION OF 5-FLUOROURACIL INTO THE NUCLEIC ACID OF TOBACCO MOSAIC VIRUS[1]

Sir:

The recent report of the incorporation of 5-fluorouracil (FU) into the nucleic acids of Ehrlich ascites tumor[2] has prompted an investigation of the effect of this compound on the production of tobacco mosaic virus (TMV). Excised disks from Turkish tobacco leaves infected 24 hours previously with the virus were floated on a 0.1% solution of FU. Under these conditions the yield of TMV was reduced by 50% as compared to a water control. The ribonucleic acid (RNA) was prepared[3] from TMV grown in the presence of 0.1% FU. Electrophoresis at *p*H 9.2 of alkaline hydrolysates of the RNA revealed an additional component which migrated more rapidly than the uridylic acids (UA) in a control hydrolysate. The spectrum (λ_{max} 266 mμ, *p*H 7) was consistent with the formulation of the material as a mixture of the 2′ and 3′ phosphates of 5-fluorouridine. The RNA was hydrolyzed with 72% perchloric acid, and the base composition was determined by two dimensional paper chromatography in isopropyl alcohol–hydrochloric acid–water[4] followed by *n*-butyl alcohol–ammonia[5] (Table I).

A FU substituted TMV-RNA labeled with P^{32} was prepared. Separate samples were hydrolyzed with snake venom diesterase and alkali. These hydrolysates were separated into 4 bands by electrophoresis at *p*H 3.5. The bands corresponding

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(5) A. Gruen and F. Kade, *Ber.*, **45**, 3367 (1912).

(6) Erich Baer, Dmytro Buchnea and Alan G. Newcombe, THIS JOURNAL, **78**, 232 (1956).

(7) Erich Baer, *ibid.*, **75**, 621 (1953).

(8) G. Marinetti and E. Stotz, *ibid.*, **76**, 1347 (1954).

(1) Aided by a grant from the U. S. Public Health Service and by a grant from the National Foundation for Infantile Paralysis.

(2) C. Heidelberger, N. K. Chaudhuri, P. Danneberg, D. Mooren, L. Griesbach, R. Duschinsky, R. J. Schnitzer, E. Pleven and J. Scheiner, *Nature*, **179**, 663 (1957).

(3) C. A. Knight, *J. Biol. Chem.*, **197**, 241 (1952).

(4) G. R. Wyatt, *Biochem. J.*, **48**, 584 (1951).

(5) W. S. MacNutt, *ibid.*, **50**, 384 (1952).

BASE COMPOSITION OF TMV-RNA's

	Substituted	Normal[8]
Adenine	1.23	1.18
Guanine	1.00	1.00
Cytosine	0.71	0.73
Uracil	.66	1.03
5-Fluorouracil	.31	

to uridylic acid were eluted and subjected to electrophoresis at *p*H 9.2 in borate buffer. The material from the diesterase digests separated into the 5′ monophosphates of uridine and 5-fluorouridine which were found in the same proportion as the corresponding 2′ and 3′ nucleotides in the alkaline hydrolysate. The 5′ monophosphates had mobilities slightly greater than those of their counterparts in the alkaline hydrolysate. In neither of these hydrolysates was there any evidence for diphosphates corresponding to end groups such as have been found in the case of 2-thiouracil[6] incorporation into TMV-RNA.

From the above data it is concluded that in TMV grown in the presence of 5-fluorouracil about one-third of the uracil in the virus is replaced by 5-fluorouracil and the total amount of TMV produced is reduced by about 50%. When applied to a local lesion host, however, the same number of lesions were produced by the substituted virus as by a normal virus. Isolated nucleic acid prepared by the detergent treatment[7] also proved to be infective.

Further work on the biological significance of these findings is in progress. The authors are indebted to the Hoffmann-LaRoche Co. of Nutley, New Jersey, for a generous gift of 5-fluorouracil.

[6] H. G. Mandel, R. Markham and R. E. F. Matthews, *Biochim. et Biophys. Acta*, **24**, 205 (1957).

[7] H. Frankel-Conrat, B. Singer and R. C. Williams, *Biochem. et Biophys. Acta*, **25**, 87 (1957).

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RECEIVED MARCH 15, 1958

THE STRUCTURE OF CRYSTALLINE POLY-(METHYL METHACRYLATE)

Sir:

A recent communication[1] described the preparation and physical properties of methyl methacrylate polymers crystallizable in three different crystal structures. Isotactic, syndiotactic and "block copolymer" chains were tentatively associated with the Type I, Type II and Type III crystal structures respectively. Type II X-ray fiber patterns show some fifty independent reflections. They have been analyzed and the major features of the crystal structure are reported here.

Eight zero layer reflections index reasonably well in the trigonal system using hexagonal axes with a = 12.17 Å. The translation identity distance corresponds to c = 10.55 Å. The calculated density is 1.23 g./ml.[3] on the basis of ten monomer units per cell. This result compares satisfactorily with the observed value of 1.22 g./ml.[3].

Reflections on the four higher layer lines destroy the trigonal symmetry. All data can be approximately indexed on a body-centered orthorhombic lattice with a = 21.08 Å., b = 12.17 Å. and c = 10.55 Å. Fine splitting of many reflections is observed, however, and the true unit cell is triclinic, pseudo-orthorhombic.

The fiber period and the density require that the polymer chains be coiled in a five-fold helix. The 5_2 helix, shown in projection in Fig. 1, accurately fits all the necessary parameters. Each circle on the circumference of the projection of the helix represents a pair of superposed backbone carbon atoms. Both the syndiotactic and the isotactic configurations fit this helix.

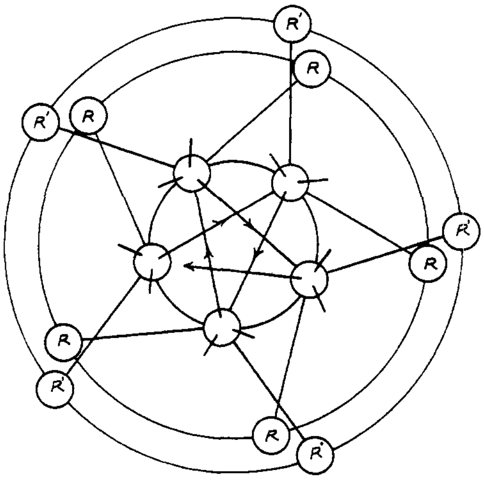

Fig. 1.—Projection of the 5_2 helix of isotactic poly(methyl methacrylate): T = 10.55 Å.; r_h = 0.75 Å.; R = CH_3; R′ = $COOCH_3$.

The five-unit two-turn helix requires the isotactic chain configuration because of the odd number of monomer units per repeat distance. A corresponding 10_4 helix would accommodate syndiotactic chains but would have twice the repeat distance (21.10 Å.). The X-ray data show no evidence for doubling the repeat period. It is, however, possible to develop chain packing arrays which would extinguish all *hkl* reflections for *l* odd. These arrays can be based upon superlattices involving right-handed and left-handed helices or on random distribution of specific dislocations.

Molecular models and calculations show that the syndiotactic 10_4 helix is stiff. This is in accord with the properties of polymers crystallizing in the Type I structure.[1] The isotactic 5_2 helix seems to be somewhat less stiff. Polymers crystallizing in the Type II structure have low glass temperatures and a relatively low melting point.[1] They are readily crystallizable and highly crystalline (*ca.* 90%). They show an extremely small specific volume change on melting.

The above considerations suggest that the Type II crystal structure is based on isotactic 5_2 helices, although interpretation of physical and thermodynamic properties in terms of chain stiffness is not yet complete. Structure refinements are in prog-

[1] T. G. Fox, B. S. Garrett, W. E. Goode, S. Gratch, J. F. Kincaid, A. Spell and J. D. Stroupe, THIS JOURNAL, in press.