

OCP has distinctive X-ray and optical properties. It contributed the "additional" lines in Carlström's³ X-ray pattern for hydroxyapatite. Single-crystal Weissenberg measurements on OCP gave the lattice constants $a = 19.7 \text{ \AA.}$, $b = 9.59 \text{ \AA.}$, $c = 6.87 \text{ \AA.}$, $\alpha \cong \beta = 90.7^\circ$ and $\gamma = 71.8^\circ$. Corresponding hydroxyapatite constants,⁷ $2a = 18.84 \text{ \AA.}$, $a' = 9.42 \text{ \AA.}$, $c = 6.885 \text{ \AA.}$, $\alpha = \alpha' = 90^\circ$ and $\gamma = 60^\circ$, resemble closely those of OCP in the values of b , c and α , which lie in the plane of the OCP plates.

Dehydration of OCP at temperatures below 180° shifted the 18.4-\AA. line progressively to lower spacings. The line disappeared upon elimination of about two-thirds of the hydrate water. The final pattern was apatitic, intermediate in sharpness between those of tooth enamel and bone. At 220° , CaHPO_4 appeared also. At 1000° , the products were $\beta\text{-Ca}_3(\text{PO}_4)_2$ and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$. Boiling water decomposed OCP into an apatite approaching hydroxyapatite in composition, along with a variable amount of CaHPO_4 . Both thermal and hydrothermal treatments sometimes yielded apatitic single-crystal pseudomorphs after OCP, the c -axes being parallel to the c of the original OCP.

Certainly a distinct crystalline compound, OCP probably has a layer-type structure, the layers perhaps closely resembling those conceivable in hydroxyapatite parallel to (10.0) but separated by water molecules. OCP is not, however, isostructural with hydroxyapatite. The two probably do not form true solid solutions but apparently form interlayered mixtures. Within the layers, the unit-cell constants of hydroxyapatite and OCP resemble those of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaClH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{Ca}_2\text{H}_7\text{K}(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$.⁸ The known ion parameters^{9,10} are also similar. Marked stability of Ca-PO_4 layers is indicated. Apatites perhaps can accommodate water, carbonates and other materials non-isomorphously between layers parallel to (10.0), thus accounting for carbonation, hydration and "internal surface"¹¹ of apatites.

The "apatite" obtained by dehydration of OCP apparently is the most acidic that has been prepared and may be another defect apatite.¹² Precipitated calcium phosphates considered as hydroxyapatite by Watson and Robinson¹³ have the morphology of either OCP or apatite pseudomorphs after OCP. The morphology of tooth and bone crystallites, as seen in their micrographs, strongly indicates that OCP is involved in the formation of these tissues, probably as a precursor that alters to apatite in place. Determinations of the crystal structures of OCP and acidic apatite thus appear requisite to an understanding of the formation and chemical properties of skeletal tissues.

Our confirmation of the presence of OCP in

(7) W. Perdok, *Schweiz. Monatschr. Zahnheilkunde*, **62**, 249 (1952).

(8) Unpublished work by TVA.

(9) G. MacLennan and C. A. Beevers, *Acta Cryst.*, **9**, 187 (1956).

(10) C. A. Beevers and B. Raistrick, *Nature* (London), **173**, 542 (1954).

(11) S. B. Hendricks and W. L. Hill, *Proc. Natl. Acad. Sci. U. S.*, **36**, 731 (1950).

(12) A. S. Posner and A. Perlof, *J. Research Natl. Bur. Standards*, **58**, 279 (1957).

(13) M. L. Watson and R. A. Robinson, *Am. J. Anat.*, **93**, 25 (1953).

dental calculus¹⁴ (apparently as a higher hydrate), along with $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and an apatite, suggests that the transitions $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{OCP} \rightarrow \text{apatite}$ occur in calculus.

(14) Segerman, quoted in ref. 12.

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PAUCIDISPERSE DEOXYRIBONUCLEIC ACID AND ITS USE IN THE STUDY OF GENETIC DETERMINANTS

Sir:

Deoxyribonucleic acid (DNA) prepared by current methods is heterogeneous with respect to both size and shape. We wish to present the results of a new technique which leads to low molecular weight, essentially monodisperse, biologically active DNA.

DNA solutions are passed at various pressures through an all-glass atomizer.¹ The molecular weight of the DNA is decreased and the distribution of sedimentation coefficients is narrowed to near monodispersity. The figure shows the sedimentation distributions² of two samples (II, III)

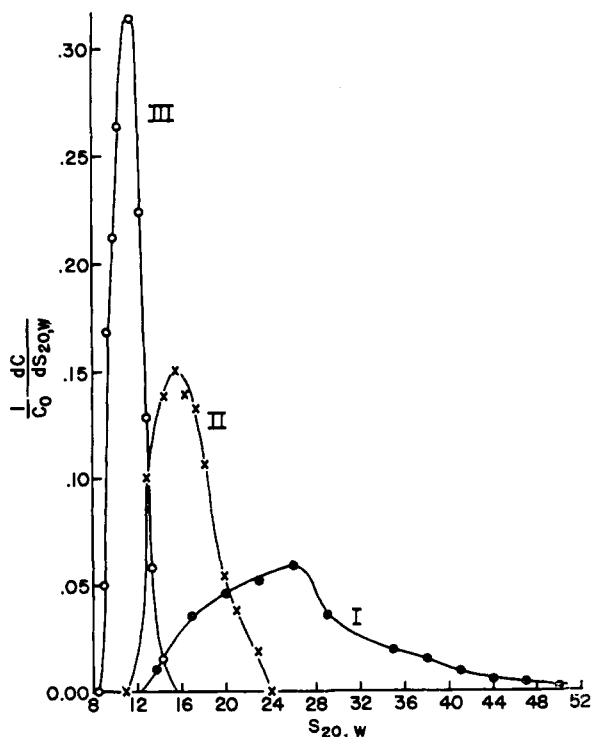


Fig. 1.—Curve I, original DNA; curve II, DNA sprayed at an intermediate rate (liquid flow, 0.1 cc./sec., air pressure, 6.6 cm.); curve III, DNA sprayed at a higher rate (see table).

(1) A stream of solution issuing from a capillary is allowed to pass through a cone of air formed from the annular space surrounding the outlet of the capillary.

(2) V. N. Schumaker and H. K. Schachman, *Biochim. Biophys. Acta*, **23**, 628 (1956).

prepared in this way from calf thymus DNA(I).³ Light scattering, intrinsic viscosity and sedimentation data are contained in the table. When the

TABLE I

LIGHT-SCATTERING, VISCOSITY AND SEDIMENTATION DATA^a

Sample	M_w $\times 10^{-6}$	$(\bar{r}^2)^{1/2}$ Å.	$[\eta]$, 100 ml./g.	$S_{20,w}$
I (original DNA)	3.3	1420	40	26
III ^b	1.2	1000	8	11

^a Determinations carried out in 0.2 M salt, 23°. Rotating cylinder viscometer used to determine $[\eta]$. A Spinco Model E ultracentrifuge equipped with ultraviolet optics was used for sedimentation data. ^b Obtained by passing DNA through atomizer eight times: rate of flow of solution, 0.2 cc./sec. (diameter of capillary, 0.015"); air pressure, 16 cm. (width of annular space, 0.013").

data for III are substituted into the equation for a flexible coil⁴

$$\frac{s[\eta]^{1/2}}{M^{2/3}} = 2.5 \times 10^6 \frac{(1 - \bar{v}\rho)}{\eta_0 N}$$

(where \bar{v} is the partial specific volume of the solute, ρ the density of the solution, η_0 the viscosity of the medium and N Avogadro's number), the calculated value of the left side is 1.95×10^{-17} , which is in excellent agreement with the theoretical value (right side) of 1.99×10^{-17} . Since the DNA is nearly monodisperse (Sample III), application of the Peterlin theory⁵ for non-Gaussian chains is justified. The persistence length is 620 Å., radius of gyration, $(\bar{r}^2)^{1/2}$, is 980 Å. (compare 1000 Å. in the table), and the contour length is 6300 Å., which is nearly identical with the value calculated from the molecular weight and a spacing of 3.4 Å. between nucleotide pairs.

The stiffness of the molecule, the 40% hyperchromic effect and the retention of transforming activity⁶ by similarly-treated pneumococcal DNA all show that these DNA samples are not "denatured"; *i.e.*, the H-bonds are intact. It is probable that the low molecular weights result from covalent bond cleavage.

Sedimentation distributions similar to those in the figure have been obtained with pneumococcal DNA containing biological markers. There is partial loss of transforming activity incurred by the spraying procedure. Theoretical calculations (to be published soon) show that the loss can be correlated with the molecular weight change to give the size of the particular genetic marker. Such results, unlike those obtained from X-ray inactivation data, are unequivocal because of the near monodispersity of the product. Further, the size of the specific determinant can be distinguished from that of the non-specific matrix in which it resides. It should be emphasized that the mechanism of transformation may require a relatively large matrix, while the various genetic functions

(3) E. R. M. Kay, N. S. Simmons and A. L. Dounc, *THIS JOURNAL*, **74**, 1724 (1952).

(4) L. Mandelkern, W. R. Krigbaum, H. A. Scheraga and P. J. Flory, *J. Chem. Phys.*, **20**, 1392 (1952).

(5) A. Peterlin, *J. Polymer Sci.*, **10**, 425 (1953).

(6) We are indebted to Dr. R. D. Hotchkiss of the Rockefeller Institute for Medical Research for these assays.

(7) L. F. Cavaliere, M. Rosoff and B. H. Rosenberg, *THIS JOURNAL*, **78**, 5239 (1956).

may be carried out by smaller units of varying size within the matrices.

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THE PROTECTIVE ACTION OF CRUDE PETROLEUM FOR METAL-PORPHYRIN COMPLEXES EXPOSED TO GAMMA IRRADIATION

Sir:

In the course of a systematic study of the properties of porphyrin compounds, several samples of porphyrins and metal-porphyrin complexes in benzene solutions, and crude oils containing metal-porphyrin complexes were subjected to high dosages of gamma irradiation. An unexpectedly high "protective" action of crude petroleum was observed. Series of tests were made in which duplicate samples, sealed in glass ampoules, were exposed to dosages of 5×10^7 r. in 18.4 hours and 7×10^7 r. in 28.2 hours in the MTR Gamma Facility of the Phillips Petroleum Co. The results are summarized in Table I.

TABLE I

DECOMPOSITION OF PORPHYRIN MATERIALS BY GAMMA IRRADIATION

Material	Concentration (micromolal)		Decomposition, %
	Orig.	Final	
Irradiation: 5×10^7 r. ^a			
Mesoetioporphyrin	124	~0	~100
Mesoporphyrin IX dimethyl ester	91.5	~0	~100
Copper-porphyrin complex (syn.)	26.3	3.1	88
Nickel-porphyrin complex (nat.)	17.3	3.9	77
Vanadium-porphyrin complex (nat.)	27.0	6.2	77
Petroleum, Okla.	345	330	4
Petroleum, Calif.	815	790	3
Asphalt, Okla. petroleum	1430	1380	3
Asphalt, Calif. petroleum	1560	1490	4
Irradiation: 7×10^7 r. ^a			
Vanadium-porphyrin complex (nat.)	16.3	<0.1	>99
Nickel-porphyrin complex (syn.)	29.8	<0.1	>99
Vanadium-porphyrin complex (syn.)	39.5	1.2	97
Vanadium-porphyrin complex (syn.) ^b	39.5	2.7	93
Vanadium-porphyrin complex (syn.) ^c	14.5	1.1	92
Vanadium-porphyrin complex (syn.) ^{c,d}	24.1	6.9	71
Petroleum, Okla.	345	305	12
Petroleum, Okla. (enriched with synthetic vanadium complex)	420	360	14

^a Sealed under atmosphere of air unless otherwise indicated. ^b Ampoule sealed inside petroleum-containing ampoule. ^c Dehydrated, deaerated, sealed under vacuum or atmosphere of nitrogen. ^d Contained 5% propane-deasphalted Oklahoma petroleum.

No appreciable differences were observed among the stabilities of the synthetic vanadium- and nickel-porphyrin complexes and those actually isolated from petroleum. In view of the sensibly