numbers because of the relatively large amounts of hydrogen gas liberated, or positive or carbonium ions or free radical centers. Space does not permit a discussion as to the relative probabilities of each of these entities being the chemically active center; such discussion will be reserved for a more detailed publication. Free radicals must be produced by the abstraction by atomic hydrogen of hydrogen from the paraffinic chains of polyethylene as well as by the incident radiation or ionization produced by the irradiation; hence it is free radicals to which this discussion will be limited.

Free radicals when first formed would presumably exist for quite long periods of time as they can disappear only by reaction with other free radicals which migrate slowly through the solid polyethylene. By a "random walk" mechanism between energetically equivalent positions, the free radical centers are postulated to move along the carbon chain until localized at the vinylidene groups where an energy state estimated to be approximately 9–10 kcal./mole lower than along the hydrocarbon chain serves effectively to trap the free radical centers. These free radical centers thus activate the vinylidene groups and cause their initial rapid disappearance.

As the disappearance of the vinylidene groups follows a zero order rate law, the evidence again shows that the incident radiation is not responsible directly for this effect. The initial disappearance of the vinylidene group is also brought about by the bombardment of polyethylene with cathode rays.[1] The effect, therefore, may be a general one.

Details of this work including a description of previous work[2] on the cross-linking and unsaturation produced in polyethylene by high energy radiations, and including an application of the postulate of this note to the work of others will shortly be submitted for publication.

Grateful acknowledgment is expressed to the Visking Corporation of Chicago for financial support of this research and to the technical staff of the Argonne National Laboratory for their coöperation.

(1) Private communication from Dr. P. H. Lindenmeyer, The Visking Corporation, Chicago.

(2) D. G. Rose, M.S. Thesis, Northwestern University, 1948; M. Dole, Report of Symposium IV, "Chemistry and Physics of Radiation Dosimetry," Army Chemical Center, Maryland, 1950, p. 120.

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STUDIES ON POLYPEPTIDES. V. THE SYNTHESIS OF ARGININE PEPTIDES[1]

Sir:

The amino acid L-arginine is a constituent of a number of biologically active polypeptides and methods for its incorporation into peptide structures are of considerable importance.

As far as we were able to ascertain the synthesis of low molecular weight L-arginyl peptides, *i.e.*, peptides in which the carboxyl group of L-arginine is linked to the amino group of another amino acid, has hitherto not been achieved.

(1) The authors wish to express their appreciation to Armour and Company and to the U.S. Public Health Service for their generous support of this investigation.

We wish to present the preparation of the first three representatives of this class of compounds, namely L-arginyl-L-alanine, L-arginyl-L-phenylalanine and L-arginyl-L-tyrosine.

Carbobenzoxy-L-nitroarginine[2] served as the key intermediate in our method of synthesis. Previous attempts to convert this substance into a hydrazide or acid chloride were unsuccessful.[3] We have now observed that carbobenzoxy-L-nitroarginine forms a mixed anhydride[4,5] when it is subjected to the action of ethyl chloroformate in the presence of a tertiary amine. This mixed anhydride reacts with amines and amino acid or peptide esters to give the respective carbobenzoxy-L-nitroarginyl amides and peptide esters. In this manner carbobenzoxy-L-nitroarginine was combined with aniline to give carbobenzoxy-L-nitroarginyl anilide, m.p. 167–168°, $[\alpha]^{27}D$ −3.5° (in CH_3OH). *Anal.* Calcd. for $C_{20}H_{24}O_5N_6$: C, 56.1; H, 5.6; N, 19.6. Found: C, 56.2; H, 5.5; N, 19.7. The interaction of the mixed anhydride with the methyl esters of L-alanine, L-phenylalanine and L-tyrosine gave: (1) carbobenzoxy-L-nitroarginyl-L-alanine methyl ester, m.p. 155–157°, $[\alpha]^{25}D$ −18.8° (in CH_3OH). *Anal.* Calcd. for $C_{18}H_{26}O_7N_6$: C, 49.3; H, 6.0; N, 19.2. Found: C, 49.5; H, 5.9; N, 19.3; (2) carbobenzoxy-L-nitroarginyl-L-phenylalanine methyl ester, m.p. 131–132°, $[\alpha]^{25}D$ −8.2° (in CH_3OH). *Anal.* Calcd. for $C_{24}H_{30}O_7N_6$: C, 56.0: H, 5.9; N, 16.3. Found: C, 55.7; H, 5.7; N, 16.1; (3) carbobenzoxy-L-nitroarginyl-L-tyrosine methyl ester, m.p. 159–160°, $[\alpha]^{25}D$ −3.5° (in CH_3OH). *Anal.* Calcd. for $C_{24}H_{30}O_8N_6$: C, 54.3; H, 5.7; N, 15.8. Found: C, 54.2; H, 5.4; N, 15.9.

Saponification with aqueous sodium hydroxide converted these peptide esters into the corresponding carbobenzoxy-L-nitroarginyl peptides, *i.e.*, carbobenzoxy-L-nitroarginyl-L-alanine, m.p. 207–208°, $[\alpha]^{26}D$ −11.6° (in CH_3OH), carbobenzoxy-L-nitroarginyl-L-phenylalanine, m.p. 225–226°, $[\alpha]^{26}D$ +1.6° (in CH_3OH) and carbobenzoxy-L-nitroarginyl-L-tyrosine, m.p. 164–166°, $[\alpha]^{28}D$ +8.3° (in CH_3OH).

Hydrogenation of the carbobenzoxy-L-nitroarginyl peptides in the presence of spongy palladium in methanol containing 10% by weight of glacial acetic acid gave the crystalline diacetate salts of the respective L-arginyl peptides, namely: (1) L-arginyl-L-alanine diacetate, m.p. 173–174°, $[\alpha]^{27}D$ +12.2° (in H_2O). *Anal.* Calcd. for $C_{13}H_{27}O_7N_5$: C, 42.7; H, 7.4; N, 19.2. Found: C, 42.9; H, 7.4; N, 19.4; (2) L-arginyl-L-phenylalanine diacetate, m.p. 172–173°, $[\alpha]^{28}D$ +23.9° (in H_2O). *Anal.* Calcd. for $C_{19}H_{31}O_7N_5$: C, 51.7; H, 7.1; N, 15.9. Found: C, 52.4; H, 7.0; N, 16.1; (3) L-arginyl-L-tyrosine diacetate, m.p. 157–158°, $[\alpha]^{27}D$ +30.4° (in H_2O). *Anal.* Calcd. for $C_{19}H_{31}O_8N_5$: C, 49.9; H, 6.8; N, 15.3. Found: C, 49.6; H, 7.2; N, 15.1. The salts exhibited a positive Sakaguchi test, gave a blue color with ninhydrin, and contained no detectable quantities of ammonium acetate.

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(3) J. S. Fruton, "Advances in Protein Chemistry," Vol. V, Academic Press, Inc., New York, N. Y., 1949, p. 64.

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A detailed description of our synthetic methods and their application to the synthesis of other L-arginyl peptides will be presented at a later date.

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THE BIOSYNTHESIS OF SUCROSE[1]

Sir:

A previous note[2] reported the formation of trehalose phosphate from UDPG[3] and glucose-6-phosphate. Following the same general procedure, an enzyme has now been found in wheat germ which catalyzes the reaction UDPG + fructose ⇄ sucrose + UDP. The evidence is as follows. The product formed was found to be non-reducing and to behave like sucrose on paper chromatography with two solvents (butanol–acetic acid[4] and ethyl acetate–pyridine[5]). After extraction of the substance from the paper followed by hydrolysis with dilute acid (5 minutes at *p*H 2 at 100°) or with purified invertase, glucose and fructose were detected chromatographically.

As shown in Table I, equal amounts of sucrose and UDP are formed in the reaction. The disappearance of UDPG and the formation of UDP were checked semiquantitatively after separation by paper chromatography with ethanol–ammonium acetate–Versene[6] as solvent.

TABLE I

The complete system contained 0.05 μmole of UDPG, 2 μmoles of fructose and 0.05 ml. of enzyme.[a] 0.1 ml. of 0.1 *M* sodium diethyl barbiturate: final volume, 0.25 ml.; *p*H 8.6; incubated during 10 minutes at 37°. The Δ values represent the difference in μmoles with a non-incubated sample.

	Δ Sucrose[b]	Δ UDP[c]	Δ Inorganic phosphate
Complete system	0.33	0.30	0.05
No UDPG	0	0	0
No fructose	0	0.05	0.04

[a] The enzyme was obtained by extracting wheat germ with three volumes of phosphate buffer 0.05 *M*, *p*H 7. After centrifuging the supernatant was dialyzed overnight cold and centrifuged again. The supernatant was precipitated twice by adding 35 g. of ammonium sulfate per 100 ml. The precipitate was suspended in water, dialyzed for 2 hours and adjusted to *p*H 5. The precipitate was redissolved in water at *p*H 7. The precipitation with acid was repeated three times. The solution contained 40 mg. of protein per ml. [b] Sucrose was estimated by the resorcinol method[7] after destroying the fructose by heating 10 minutes at 100° in 0.01 *N* NaOH. [c] Determined enzymatically.[2]

The same chromatographic procedure was used for studying the reversibility. Starting with UDP and sucrose it was found that UDPG is formed. Its identity was checked by extracting it from the paper and measuring the coenzymic activity on galactowaldenase.[8] The data indicate that the equilibrium is displaced in favor of sucrose synthesis.

No sucrose formation or UDPG disappearance was found to occur if glucose-1-phosphate was added instead of UDPG, or if sorbose, aldoses, arabinose or the 1- or 6-phosphates of fructose or glucose were substituted for fructose.

Although sucrose had been previously obtained by enzymic action, the mechanism of the synthesis in plants remained obscure. The enzyme which Doudoroff and Hassid extracted from *Pseudomonas saccharophyla* catalyzes the formation of sucrose from glucose-1-phosphate and fructose, but it has not been possible to detect such a reaction in plant material.[9] The enzyme described in this paper has been found to be present not only in wheat germ but also in corn and bean germs and in potato sprouts. Tests for UDPG by its coenzymic activity gave positive results on wheat germ extracts.

Moreover, Buchanan, *et al.*[10] have published evidence of the presence of UDPG in other plants. They also suggested that it was involved in sucrose synthesis, probably by reacting with fructose phosphate to give sucrose phosphate. The latter substance can be excluded as an intermediate in the reaction catalyzed by the wheat germ enzyme because the product is all free sucrose and only negligible amounts of inorganic phosphate are released (Table I).

(1) This investigation was supported in part by a research grant (G-3442) from the National Institutes of Health, United States Public Health Service, and by the Rockefeller Foundation.

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(3) The abbreviations UDPG for uridine diphosphate glucose, and UDP for uridine diphosphate are used.

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CONFIGURATIONS OF LIGANDS HAVING INTERNAL ROTATION AXES IN COÖRDINATION COMPOUNDS

Sir:

Considerable evidence based on spectroscopic, thermal and electric measurements has been accumulated to indicate that 1,2-disubstituted ethanes, XH_2C-CH_2X, exist in *trans* and *gauche* configurations in the gaseous and liquid states and in solutions, but they exist only in *trans* configuration in the solid state.[1] Our infrared measurements on ethylene thiocyanate have also shown that this substance exists in the *trans* and *gauche* configurations in chloroform solutions but it exists only in *trans* configuration in the solid state. The spectrum of the complex $[PtCl_2(CH_2SCN)_2]$ has been found to be quite similar to that of the *gauche* configuration of ethylene thiocyanate but quite different from that of the *trans* configuration. Therefore, the configuration of this chelate ligand in the co-

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