

principal equatorial reflection. Density requires about 21 amino-acid residues along 20 Å. of helix axis.<sup>4</sup> The 7 nearly equivalent groups should, therefore, comprise 3 residues each.

The above analysis does not determine uniquely the chemical connection of the residues. Primitive helical connection has the merit of allowing several-fold chain extensibility from the average 0.95 Å. of axial projection per residue.<sup>4</sup> Intensity relationships and stereochemical considerations are being used to derive detailed models.

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### REACTIONS OF ALIPHATIC AMINES WITH SUGARS\*

Sir:

We have found that reactions of long-chain primary aliphatic amines with sugars can go far past the amine glycoside stage. In our work as many as five or six moles of amine have reacted with one mole of hexose sugar. In effect, these reactions are replacement of hydroxyl groups by alkylamino groups. The actual mechanism of the reaction, however, is probably a series of Amadori rearrangements, each followed by reaction of the carbonyl group so formed with another mole of amine.

Ketoses appear to be more reactive than aldoses toward amines. In general, formation of amine glycosides takes place very readily at room temperature. A solution of equimolar amounts of fructose and octadecylamine in aqueous isopropyl alcohol, however, reacts in a day or two to give a good yield of a white solid, m.p. 105.5–106.2° (dec.). Elementary analysis shows that this compound is formed from two moles of amine and one of fructose by loss of two moles of water. From this fact it is clear that the product is not an aldehyde-ammonia type of compound or a mixture of amine and amine glycoside.

*Anal.* Calcd. for C<sub>42</sub>H<sub>86</sub>N<sub>2</sub>O<sub>4</sub>: C, 73.81; H, 12.69; N, 4.10. Calcd. for C<sub>42</sub>H<sub>88</sub>N<sub>2</sub>O<sub>5</sub>: C, 71.92; H, 12.65; N, 4.00. Found: C, 74.36; H, 12.52; N, 4.29.

To obtain a similar product with glucose it is necessary to use an excess of amine and it is desirable to heat the mixture. By increasing the severity of the reaction conditions, one may introduce still more amino groups. A solution of six moles of octadecylamine and one mole of glucose in aqueous isopropyl alcohol, heated several hours at 60–70°, yields a yellow solid, m.p. 66.5–68°, derived from four moles of amine and one of sugar.

*Anal.* Calcd. for C<sub>78</sub>H<sub>160</sub>N<sub>4</sub>O<sub>2</sub>: C, 78.96; H, 13.60; N, 4.72. Found: C, 78.66; H, 13.37; N, 4.41.

This octadecylamine-glucose product forms a monopicate of uncertain m.p. (ca. 50–95°).

*Anal.* Calcd. for C<sub>84</sub>H<sub>163</sub>N<sub>7</sub>O<sub>9</sub>: C, 71.29; H, 11.61; N, 6.93. Found: C, 71.83; H, 11.77; N, 6.70.

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Five moles of octadecylamine react with one mole of sorbose on extended heating in alcohol to give a tan solid, m.p. 67–69.5°.

*Anal.* Calcd. for C<sub>98</sub>H<sub>197</sub>N<sub>5</sub>O: C, 80.19; H, 13.81; N, 4.87. Found: C, 80.24; H, 13.25; N, 4.79, 4.53.

This sorbose-octadecylamine product forms a yellow monopicate, m.p. 45–47°.

*Anal.* Calcd. for C<sub>102</sub>H<sub>200</sub>N<sub>8</sub>O<sub>8</sub>: C, 73.50; H, 12.10; N, 6.72. Found: C, 72.95; H, 11.43; N, 6.73.

These findings suggest new approaches to the study of the browning reaction. A more detailed report on this work will be published later.

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### THE FREE AMINO GROUPS OF $\gamma$ -GLOBULINS OF DIFFERENT SPECIES

Sir:

Porter<sup>1</sup> has found that normal rabbit  $\gamma$ -globulin and the specific rabbit antibody to hen's ovalbumin possess the identical N-terminal peptide sequence (Ala.Leu.Val.Asp.Glu-). It has been suggested that this is in agreement with theories of antibody formation which ascribe specificity to specific surface configuration rather than to differences in amino acid sequence or composition. In contrast are earlier findings by many investigators<sup>2</sup> which have shown that human, bovine and equine  $\gamma$ -globulins are heterogeneous by a variety of criteria. We now wish to report a study of the free amino groups of these globulins by reaction with dinitrofluorobenzene to form the dinitrophenyl (DNP) derivatives by the procedure of Sanger. The present results indicate differences among preparations of human  $\gamma$ -globulins and considerable species variation (Table I).

TABLE I  
NUMBER OF FREE AMINO GROUPS IN VARIOUS  $\gamma$ -GLOBULINS

	Human II-1,2	Human II-3	Human cryoglobulin	Bovine A
Asp (60%) <sup>a</sup>	1.06	1.01	1.3	0.13
Ser (81%)	.10	.17	<sup>c</sup>	.09
Glu (56%)	1.82	1.06	1.2	.15
Ala (55%)				.09
Val (57%)				.11
Lys (90%)	75	74	70	73
Lys <sup>b</sup>	79	69		74

<sup>a</sup> Parentheses give recovery values for DNP amino acids after hydrolysis for 24 hours in a sealed tube at 105°. The tabulated values are based on these recoveries, and on an assumed molecular weight of 160,000 for all these proteins. Data on II-1,2 and II-3 globulins are the averages of five determinations each. The cryoglobulin values are averages of three determinations and the bovine, of four independent measurements. <sup>b</sup> Values calculated from microbiological assays. <sup>c</sup> None detectable.

The results on the II-1,2 and II-3 fractions suggest the presence of two or more distinct molecules with different N-terminal residues. The "cryoglobulin" is a  $\gamma$ -globulin from a patient with multiple

(1) R. R. Porter, *Biochem. J.*, **46**, 473 (1950).

(2) E. L. Smith and B. V. Jager, *Ann. Rev. Microbiol.*, **6**, 207 (1952).