

stoichiometric and the rate controlling step is the unimolecular dissociation of pentaphenyl-ethane into free radicals. A four-step mechanism for the capture of the organic radicals by nitric oxide has been proposed. Since the overall reaction is quantitative and irreversible in the

absence of additives and since the fate of the radicals is known nitric oxide possesses unusual advantages as a reagent for studying the rates of dissociation of organic compounds at elevated temperatures.

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RECEIVED NOVEMBER 24, 1941

[CONTRIBUTION FROM THE LABORATORIES OF DITTO, INC.]

Mechanical Influence upon Tanning

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The aldehyde content in human blood is so high,¹ that in the light of experience with industrial protein gels, it should amply suffice to tan the body proteins to complete rigidity and loss of elasticity within a matter of months. While such progressive tanning is evidenced by the loss of elasticity of tissues such as for example the arteries^{2,3} with aging, the rate of this tanning is much less than one would expect in view of the tanning substances present in body fluids.

Therefore, it appeared that this tanning might be retarded by factors not previously considered, and that a study of progressive tanning of protein gels during rhythmical motion simulating that of living arteries, might yield information bearing on this subject. The present investigation was made with this aim in view.

Since high Bloom gelatins are protein substances obtained by the mildest type of extraction, and since their behavior when tanned with slight amounts of tanning agents has been most thoroughly studied and understood,⁴ this protein was selected for our initial study.

300 grams of 225 Bloom pig skin gelatin was allowed to swell in a mixture of 300 g. of glycerol and 450 g. of water, at room temperature. After one hour, the mixture was melted in a water-bath of 55° and mixed with 1500 g. of additional glycerol, pre-warmed in the same water-bath.

The resultant mix was divided in two 50% aliquots. To one of these we added 60 cc. of 33% acetaldehyde solution, as tanning agent; the other aliquot served as our non-tanned control.

The mixes were allowed to stand one-half hour at 55°, to eliminate air bubbles, and were then poured to form uniform sheets having the dimensions 330 mm. × 216 mm. × 2.5 mm. Two such sheets were obtained from each aliquot.

(1) K. Ri, *J. of Bioch., Tokyo*, **32**, 38-50 (1940).

(2) J. C. Bramwell, A. V. Hill and B. A. McSwiney, *Heart*, **10**, 233 (1923).

(3) J. M. Steele, "Abstracts of the Atlantic City Meeting of the American Chemical Society," September, 1941, p. B2.

(4) J. Bjorksten, *Chem. Ind.*, **48**, 749 (1941).

The sheets were allowed to stand for twenty hours at room temperature, in order to give them the firmness required.

After this period, one tanned and one non-tanned sheet were attached with one short end to a rigid metal holder, and with the other short end to a holder having a reciprocating motion, so that the sheets were continually stretched and relaxed at a rate of eight times per minute, to an extent of 10% elongation.

The other two sheets, one tanned and one non-tanned, were placed on a porous backing next to the stretching machine, and were thus exposed to room temperatures, humidities and ventilation identical with those of the stretched samples.

After twelve days, the stretching was interrupted, the sheets were kept overnight (sixteen hours) at 55% relative humidity and 21°. Test strips were cut from center and ends of each sheet having their length parallel to the direction of stretch, and others perpendicular thereto, and the tensile strength was determined in a conventional paper tensile strength testing machine.

The tabulated figures are averages of triplicate determinations, all of which were within 5% of the averages shown.

TABLE I
TENSILE STRENGTH IN GRAMS PER SQ. MM.

| | | In direction of stretch | Across direction of stretch |
|--------------------------------|------------------------|----------------------------|--------------------------------|
| Stretched | End | 171 | 144 |
| | Center | 192 | 146 |
| Stretched non- | End | 153 | 148 |
| | tanned sheet Center | 150 | 152 |
| Tanned non-stretched sheet | | 60 | |
| Non-tanned non-stretched sheet | | 155 | |

With the stretched sheets, determinations were made at the end and the center of each sheet, as the direction of stretch might have shown slight deviations near the edges.

The most striking facts shown by these data are: (I) that the stretched tanned sheet not only is vastly stronger (320%) than the non-stretched tanned sheet in the direction of stretch, but also in the direction perpendicular to the tension

(240%); (II) that the stretched tanned sheet is materially stronger in the direction of stretch than is the non-tanned sheet; (III) that in the non-tanned sheets there is no correlation between strength and direction of stretch, while in the tanned sheets this correlation is pronounced; (IV) that in the non-tanned sheets, stretching did not cause any observable increase in strength.

Since the strength of the stretched tanned sheet was several times greater than that of the non-stretched tanned sheet, it appeared advisable to investigate whether the tanning itself had been impeded by the stretching process. For this purpose, the softening points of the sheets were determined on circular samples of 25 mm. diameter, by the Ring and Ball method, in oil-bath.

The softening points of both of the non-tanned sheets were $60 \pm 1^\circ$, while those of the stretched as well as the non-stretched tanned sheets exceeded 110° .

The elongation of the stretched sheets at the termination of the test was approximately 5%, and was thus insignificant in relation to the effects observed.

The condition of the gel sheet tanned without stretch was representative of similar gels tanned to a softening point exceeding 110° , regardless of the tanning agents employed, but the strength and elasticity of the stretched and tanned sheets far exceed anything the authors have ever seen in such gels having a softening point above 100° in their many years of experience with industrial protein gels of this general formulation. The

high softening point conclusively proves that the tanning agent remained and was active in the tanned stretched sheets. Manifestly the continued stretch exerted a directional influence on the positioning of tanning bridges in relation to the protein molecules, so that the tanning bridges connecting the protein molecules were formed in positions not interfering with stretch and relaxation of the gel.

The condition of repeated stretching and relaxation is even present in the walls of the arteries of higher animals. The effect described above may be of considerable importance in delaying the aging of arteries, and may at least in part explain the slow progress of this aging in spite of the well-known presence of active tanning agents in the blood stream. The effect may also be a factor contributing to the beneficial effects of exercise, and to the atrophy of organs under conditions of continued absence of stretch.

Further work is in progress.

Summary

Rhythmical stretching and relaxation of a protein gel containing a tanning agent, caused a very great increase of tensile strength over a similarly tanned non-stretched gel, *in all directions in the gel*. The effect did not take place in the absence of the tanning agent. The softening point of the stretched gel rose as in normal tanning.

Analogies with conditions in human arteries are discussed.

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RECEIVED NOVEMBER 10, 1941

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF MERCK & CO., INC.]

N-Allylnormorphine

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In a recent note McCawley, Hart and Marsh¹ described the preparation and properties of N-allylnormorphine, which appears to be the first N-substituted normorphine derivative to be reported. Our many efforts to repeat the preparation as outlined in this note have failed.

We have found that normorphine reacts readily with allyl bromide in the presence of chloroform at 110° . The properties of the product and of its hydrobromide are entirely different from those

reported by McCawley, *et al.* That the N-allylnormorphine structure should be assigned to our product was proved by converting it into N-allylnorcodeine according to Rodionov's method.² A comparison of our N-allylnorcodeine with a sample synthesized from norcodeine by the procedure of von Braun³ indicated that the two were identical.

The normorphine used in our investigation was prepared by the method of von Braun,⁴ as well as

(1) McCawley, Hart and Marsh, *THIS JOURNAL*, **68**, 314 (1941).

(2) Rodionov, *Bull. soc. chim.*, **39**, 305 (1926).

(3) von Braun, *Ber.*, **49**, 977 (1916).

(4) von Braun, *ibid.*, **47**, 2312 (1914).