TABLE I.
Gold Numbers of Various Emulsoid Colloids.

Substance.	Gold number. Gortner.	 Zsigmondy.[a]
Dextrin (British gum)	125–150	
Soluble starch	10–15	
Sodium oleate	2–4	0.4–1.0
Egg albumen	0.08–0.10	0.15–0.25 (Taylor[b])
Gum arabic	0.10–0.125	0.15–0.25
Protalbinic acid	0.15–0.20	0.03–0.08 (sodium salt)
Lysalbinic acid	0.10–0.125	0.02–0.06 (sodium salt)
Gelatin	0.005–0.0125	0.005–0.010

[a] R. Zsigmondy and E. B. Spear, *loc. cit.*

[b] Taylor, *loc. cit.*

under investigation, and that be the case, we must conclude that the *protective action of Paal's protalbinic and lysalbinic acids, as measured by the gold number, has been much over-rated, inasmuch as their gold number is only approximately equal to that of gum arabic and only about* $^1/_{10}$ *that of gelatin.*

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[CONTRIBUTION FROM THE ESSENTIAL OILS LABORATORY, DRUG DIVISION, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE CONSTITUTION OF CAPSAICIN, THE PUNGENT PRINCIPLE OF CAPSICUM. II.

BY E. K. NELSON.

Received December 31, 1919.

Since the appearance of the author's first communication[1] on this subject, Lapworth and Royle[2] have published the results of their work on capsaicin. These investigators are not fully disposed to accept the author's view of the constitution of capsaicin as final, on the ground that "his (Nelson's) conception of capsaicin as an acid amide is not easily reconciled with the somewhat ready reduction of a part of capsaicin to ammonia and an aliphatic alcohol boiling at about 216–217°; its distinctly, basic character and the great stability of the substance toward alkalies are also somewhat difficult to understand." They surmize that "under the energetic conditions used by Nelson internal oxidation or molecular rearrangement would not be surprizing."

Proof of the structure of capsaicin is now given by its generation from synthetic vanillyl amine and the decenoic acid previously isolated from capsaicin. The complete synthesis is impossible, of course, until we know the exact structure of the decenoic acid entering into the molecule. In view of the great number of possible isomers and the difficulty

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[1] THIS JOURNAL, 41, 1115 (1919).

[2] *J. Chem. Soc. Trans.*, 115, 1109 (1919).

of locating the double bond in a substance of which only limited quantities are available, the structure of this decenoic acid must remain at present undetermined.

Regeneration of Capsaicin.

5.1 g. of decenoic acid (from capsaicin) was converted into the acid chloride by means of phosphorus trichloride and the acid chloride added gradually to a suspension of 9.2 g. of vanillyl amine in dry ether. 5.5 g. of a crystalline, very pungent substance was obtained, which recrystallized from a mixture of petroleum ether with 10% of ether, melted at 65°, and, mixed with capsaicin, showed no depression in melting point. An optical-crystallographic examination by Dr. E. T. Wherry, of this bureau, also showed it to be identical with capsaicin.

Calc. for $C_{18}H_{27}NO_3$: C, 70.8; H, 8.8. Found: C, 70.5; H, 9.0.

Capsaicin must, therefore, be a vanillyl decenoyl amide.

Vanillyl octoyl amide[1] was boiled for 2 hours with a 50% solution of sodium hydroxide and recovered unchanged. It is somewhat soluble in conc. hydrochloric acid and is precipitated unchanged on the addition of water.

Free vanillyl amine is quite unstable, ammonia being easily liberated from it by boiling with water or solutions of alkali carbonates. Therefore, in an alkaline reduction process, such as the boiling with sodium in ethyl alcohol performed by Lapworth and Royle, any decomposition of the capsaicin taking place would probably result in the liberation of ammonia.

Decenoic Acid.

Attempts to oxidize the decenoic acid from capsaicin by means of chromic acid mixture indicated that several acids may be formed. Owing to the small amount of acid used, no very definite results were obtained.

Fusion with potash splits decenoic acid into acetic acid and an octoic acid. However, this affords no proof of the location of the double bond, as it is well known that potash fusion may cause a displacement of the double bond in unsaturated acids. Acetic acid was identified through its silver salt and the formation of ethyl acetate. The octoic acid obtained has an odor like that of caprylic acid, but differs from the latter in that it remains liquid when cooled in an ice and salt mixture, and boils at about 240–245°. Its silver salt was prepared and found to be difficultly soluble in water.

Calc. for $C_8H_{15}O_2Ag$: Ag, 43.0; C, 38.2; H, 6.0. Found: Ag, 42.6; C, 38.6; H, 5.8.

Summary.

Confirmation of the structure of capsaicin has been obtained by its regeneration from vanillyl amine and the decenoic acid isolated from capsaicin. Synthetic vanillyl octoyl amide was found to resemble cap-

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[1] Nelson, This Journal, 41, 2124 (1919).

saicin closely in its stability toward boiling conc. sodium hydroxide solution and in its solubility in conc. hydrochloric acid.

The decenoic acid isolated from capsaicin, on fusion with potassium hydroxide, breaks down into acetic acid and an octoic acid with a branched chain.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE USE OF OXALYL CHLORIDE AND BROMIDE FOR PRODUCING ACID CHLORIDES, ACID BROMIDES OR ACID ANHYDRIDES. III.

BY ROGER ADAMS AND L. H. ULICH.

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It has already been pointed out in previous communications that oxalyl chloride in the presence of pyridine[1] is a valuable reagent for the identification of phenols and that its action with aromatic acids[2] offers a simple method for the preparation of the corresponding anhydrides. This paper contains an extension of the work with oxalyl chloride. The reactions of this substance with various aliphatic and aromatic acids as well as with the sodium salts of such acids are described. Either acid anhydrides or acid chlorides may be obtained, depending upon the conditions and proportions of materials used. Aliphatic and aromatic acid anhydrides and oxalyl chloride give the corresponding acid chlorides. The mechanism of these various reactions is explained. It has been shown also that oxalyl chloride may be used for producing certain inorganic acid chlorides from the corresponding oxides, and for causing the Beckmann rearrangement of various ketoximes. Oxalyl bromide may be employed in the same way as oxalyl chloride and yields with acids or their salts either acid anhydrides or acid bromides. Phosphorus pentabromide and organic acids or phosphorus pentabromide and the salts of organic acids yield acid bromides.

If aromatic or aliphatic acids are warmed with 2.5 moles of oxalyl chloride, these acids are converted quickly and practically quantitatively into the corresponding acid chlorides. The reaction may even be carried out in the presence of benzene as a solvent and very successful results obtained. Various types of acids were chosen for experimentation. The following give excellent yields of acid chloride: benzoic, *p*-bromobenzoic, *o*-bromobenzoic, *n*-valeric, lauric, phenylacetic, hydrocinnamic and salicylic acids. *p*-Hydroxybenzoic acid does not give an acid chloride but instead a complex condensation product. Certain nitro derivatives of benzoic acid react very peculiarly with oxalyl chloride; thus *m*-nitro-

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[1] THIS JOURNAL, 37, 2716 (1915).

[2] *Ibid.*, 40, 424 (1918).