Summary

The reactions of sodium chloroacetate and sodium nitrite have been studied and it has been ascertained that in using molecular quantities of the reactants approximately 50% of the nitrite is converted into nitromethane, while about 24% of it gives nitromethane which undergoes further condensation to what is presumably the sodium salt of methazonic acid. About 26% of the sodium nitrite does not react, chiefly because 15% or more of the sodium chloroacetate undergoes hydrolysis to sodium glycolate. The formation of nitromethane may be increased to approximately 75% of the theoretical amount if a sufficient excess of sodium chloroacetate is used to insure the complete reaction of the sodium nitrite. The actual yields of nitromethane obtained were about 9% lower than those given above (50 and 75%) because of mechanical losses on the scale of operation used in obtaining them. The weight of nitromethane actually obtained may be increased by about 10% by modifying the standard method so that the sodium chloroacetate is introduced into the nitrite solution after the latter has been heated to the temperature of reaction.

A method is described for the determination of sodium nitrite in the presence of nitrates and methazonic acid and its condensation products.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE RESEARCH LABORATORY IN ORGANOTHERAPEUTICS, ARMOUR AND COMPANY]

GEOGRAPHIC LOCATION AND THE IODINE CONTENT OF THE THYROID GLAND

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The biochemical literature contains but very limited data regarding seasonal fluctuations in any physiological function. We know that the thyroid gland needs iodine to render its secretion active. The amount of iodine in the gland consequently reveals its potency. Seidell and Fenger[1] have shown that a very marked seasonal variation exists in the percentage of iodine present in the healthy, normal thyroid glands of domestic animals. There is, in general, from two to three times as much iodine present in the glands during the summer and fall months as during the winter and spring seasons. The glands on which these conclusions were based were collected at Chicago and represented principally the middle central states.

As a result of an inquiry from Dr. W. L. Aycock of the Harvard Medical School, it was decided to investigate existing conditions in the northern and southern portions of the United States. Hog glands were selected

[1] Seidell and Fenger, *J. Biol. Chem.*, 13, 517 (1913), and Bulletin 96, Hygienic Laboratory, U. S. Public Health Service, 1914, p. 67.

because the hog is an omnivorous animal like the human race, and because the size of the hog thyroid remains constant throughout the seasons.

Approximately one pound of hog thyroid glands was collected weekly, with a few exceptions, for a period of one year at West Fargo, N. D., our most northern abattoir, and also at Fort Worth, Texas, our most southern plant. Immediately after dissection, the glands were frozen and shipped to Chicago in this condition. On arrival, the glands were thawed out, carefully freed from extraneous tissue and weighed. The glands were next finely minced and dehydrated *in vacuo* at low temperature (85°F.). The fat was removed by means of petroleum ether and the desiccated fat-free material powdered. On the finished powder we determined the ash, P_2O_5 and iodine. Lack of space permits only the showing of the iodine values.

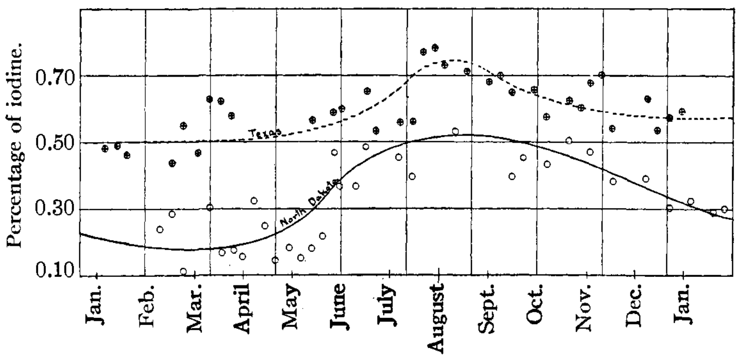

Fig. 1.—Seasonal variation in iodine content of hog thyroid glands from Texas and North Dakota, 1929–30.

Disregarding fluctuations due to the comparatively small number of glands constituting each weekly sample, it will be seen from the chart that both types of glands show seasonal variations in the form of a marked iodine increase during the summer months. The iodine level is higher in the southern than in the northern thyroids but the seasonal fluctuation is more pronounced in the northern glands. The yearly average for the Texas glands is 0.60% iodine with a maximum of 0.78% in August and a minimum of 0.44% in the latter part of February, while that of the North Dakota thyroid is only 0.32% iodine with a top peak at 0.53% in August and a low dip down to 0.13% early in March.

The weight of the fresh glands is not tabulated in this communication. It was found, however, that the fresh southern thyroids were smaller throughout the year and weighed approximately 20% less than the northern glands. The amount of thyroid iodine per unit of body weight is, in spite of this difference, considerably higher in the Texas hogs than in the North Dakota animals. The principal reason for this condition must be sought in the geographic location of the two collection points. The latitude of West Fargo is about 47° north and the winters are quite severe. Fort Worth is situated close to the thirty-third parallel and the winter months are comparatively mild.

Conclusions

Calculated on the desiccated fat-free basis, the yearly average for hog thyroid glands from North Dakota is 0.32% iodine, while that of Texas glands is 0.60% iodine.

The seasonal variation in the iodine content is most pronounced in the northern glands.

The higher iodine level of the Texas glands and the greater seasonal fluctuations of the North Dakota thyroids are attributed to the geographic location of the two states.

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THE ACETYLATION OF ORTHO-HYDROXY ALDEHYDES

BY T. MALKIN AND M. NIERENSTEIN

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Herzig and Wenzel[1] found that when phloroglucin aldehyde is heated with acetic anhydride and anhydrous sodium acetate, no trace of the corresponding coumarin was produced, and that the condensation product consisted mainly of 2,4,6-triacetoxybenzylidenediacetate (I), which melted at 155–156°. Later, Knoevenagel[2] showed that benzylidenediacetate formation is general to all aromatic aldehydes, being favored by rise of temperature. On the other hand, Pratt and Robinson[3] apparently succeeded in preparing for the first time triacetylphloroglucin aldehyde (II) by the interaction of phloroglucin aldehyde with acetic anhydride and anhydrous potassium carbonate. They found that during the reaction considerable heat was evolved and that the resulting product melted at 151°, a melting point subsequently raised to 156–157° by Robertson and Robinson.[4] The agreement between the melting points found by Herzig and Wenzel and Robertson and Robinson, respectively, for the two substances I and II seemed to us very striking, and since Robinson's triacetylphloroglucin aldehyde is an important starting material in the syntheses of a large number of the anthocyanidins,[5] we thought it desirable to

[1] Herzig and Wenzel, *Monatsh.*, **24**, 864 (1903).

[2] Knoevenagel, *Ann.*, **402**, 115 (1913).

[3] Pratt and Robinson, *J. Chem. Soc.*, **127**, 1184 (1925).

[4] Robertson and Robinson, *ibid.*, 1713 (1927).

[5] See Pratt and Robinson, *J. Chem. Soc.*, **127**, 1182 (1925); Malkin and Robinson, *ibid.*, **127**, 1190 (1925); Gatewood and Robinson, *ibid.*, 1959 (1926); Nolan and Robinson *ibid.*, 1968 (1926); Robertson and Robinson, *ibid.*, 1710 (1927); Malkin and Nierenstein, *Ber.*, **61**, 791 (1928).