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PREPARATION OF TYROSINE FROM STEFFEN'S WASTE

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In the search for substances, other than glutamic acid, betaine, and potassium chloride, that might be obtained from Steffens waste, a quantity of concentrated waste, sp. gr. 1.4, was diluted with an equal volume of water, boiled with a small amount of activated carbon, and filtered. A precipitate which formed on cooling was identified as l-tyrosine. Though it had been found in beet molasses, it is apparently the first time that tyrosine has been obtained from Steffen's waste.

In 1846, Justus von Liebig discovered tyrosine in cheese (3). Since then it has been found in many substances containing proteins. v. Lippman (4) 1884 obtained tyrosine from beet sugar molasses. His method involved the use of alcohol, sulphuric acid, basic lead acetate, and hydrogen sulphide. No yield was given. Our method is much simpler.

Properties: Tyrosine, or p-hydroxyphenylalanine, ($0HC_6H_4$-$CH_2CHC00H)NH_2$, occurs in nature in the levo-form $[\alpha]^{20}D =$ $-8.64°$ using 3.9 g. per 100 ml. of 5.5 N HC1 (2). It crystallizes in fine needles that appear as sheaves under the microscope. One part is soluble in 2940 parts of water at 17°C. It is the most insoluble of the amino acids. It forms soluble acid or basic salts. It is only sparingly soluble in acetic acid. It gives a positive reaction to Millons test and forms tyrosine hydantoin with KCN0.

EXPERIMENTAL

After preliminary experiments using 250 grams and 1000 grams of concentrated waste, (sp. g. 1.4), from Mason City, Ia., an experiment was made on a larger scale.

6.8 kilograms of Steffens waste, (sp. g. 1.4), from Mason City, which had been concentrated at the factory, was diluted with 2500 ml. of water to a sp. g. of 1.275. This solution was warmed with 150 grams of carbon and filtered hot. The paH of the filtrate was adjusted to 5.7, the isoelectric point of tyrosine, by the addition of 540 ml. of concentrated hydrochloric acid (1.18-1.20). Tyrosine precipitated. The precipitate and liquid thoroughly cooled, filtered, and the tyrosine washed with cold water. It was recrystallized by

dissolving in hot dilute NaOH, then, with rapid stirring, adding almost the amount of HCl calculated to neutralize the NaOH, and an excess of glacial acetic acid, in which tyrosine is only slightly soluble. After cooling, the tyrosine was filtered off and washed free from chloride with ice water. Yield = 35.2 g. or 0.5 per cent.

A portion of this tyrosine was recrystallized twice more from hot water, dried in a vacuum desiccator, and nitrogen determined by the micro Kjeldahl and micro Dumas methods. The amount found agreed with the amount calculated for tyrosine, $C_9H_{11}O_3N$.

	Calcd. for $C_9H_{11}O_3N$:	Found:
Micro Kjeldahl	7.73 per cent	7.91 per cent
Micro Dumas	7.73 per cent	7.70 per cent

Preparation of Tyrosine and Glutamic Acid. Glutamic acid can be obtained after the removal of tyrosine. It is unnecessary to concentrate to a sp. g. of 1.4 and dilute to a sp. g. of 1.275. The most economical procedure is to concentrate to a sp. g. of 1.275, remove tyrosine, and obtain glutamic acid.

Experiment: 4200 g. of dilute waste was concentrated to a sp. g. of 1.275, treated by a combination of the methods given for tyrosine and glutamic acid. The hydrochloric acid used was proportioned to the concentration of the waste. The yield of tyrosine was 0.45 per cent and of glutamic acid, 4.7 per cent.

Optically Active Features of Tyrosine Obtained from Steffens Waste

The specific rotation of several samples of tyrosine obtained from Steffens waste was uniformly low. After three recrystallizations, one sample had a constant value, $[\alpha]^{20}D = -5.12°$. 3.9 g. was dissolved in 100 ml. of 5.5 N HCl. The recorded value is $[\alpha]^{20} D = -8.64°$.

This tyrosine, converted to the hydantoin, had a specific rotation $[\alpha]^{20} D = -91.6°$. 1.86 g. was dissolved in 100 ml. N NaOH. The recorded value under these same conditions is —143° (1).

To prove that the tyrosine might have been partially racemized during the concentration of the alkaline waste, 10 gallons of dilute waste was acidified with sulphuric acid and concentrated. Tyrosine was obtained in the usual way and after one recrystallization gave a value of $[\alpha]^{20} D = -8.32°$. The hydantoin derivatives gave a value of $[\alpha]^{20} D = -142.5°$. Tyrosine evidently under-

goes partial racemization during the concentration of the waste as ordinarily carried out.

SUMMARY

Steffen's waste is a potential source of large amounts of tyrosine. Four thousand tons of concentrate, sp. g. 1.3, were obtained at the beet sugar factory at Mason City, Ia. On the basis of our yields, this is equivalent to about sixteen tons of tyrosine annually.

We would like to find uses for typrosine.

Unless the dilute waste is acidified, tyrosine from Steffens waste is partially racemized during concentration.

Glutamic acid can be obtained after the removal of tyrosine.

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