Determination of Glycerol.—This was carried out by the method of Reeves,[17] in which the vicinal glycol is oxidized with periodic acid, and the formaldehyde from terminal carbinol groups collected and weighed as the dimedone complex.

Determination of Radioactivity.—All counting was carried out on stainless steel plates, in a gas flow counter, in the proportional range. The counter efficiency was about 45%.[18]

Formaldimedone from the glycerol determination, particularly in the case of the α-labelled glycerol, was recrystallized twice from ethanol–water, centrifuged down, and plated from 30% alcohol. In order to obtain uniform plates, two or three drops of 95% ethanol were added to the material on the plate. The formaldehyde from the periodate oxidation was also distilled off, oxidized with $KMnO_4$, and counted as $BaCO_3$. The formic acid from the β-carbon of glycerol was oxidized with HgO to CO_2 and similarly counted.[19]

Combustion of Glycerol Samples.—These were combusted and their carbon content determined by the method of Van Slyke and Folch[20] with modifications in the reagents and apparatus.[21,22] The carbon dioxide was recovered and converted to $BaCO_3$ for counting.[23]

Paper Chromatograms.—These were carried out by the method of Hough.[9] The R_f values observed with several solvent systems were similar to those reported by that author. Up to 2 mg. of glycerol in solution was applied to each strip in a small spot by successive applications and evaporations with a hair-drier. The chromatograms were allowed to run for 18 hours.

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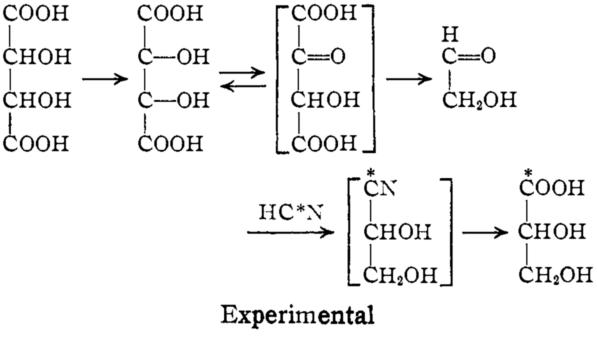
[CONTRIBUTION FROM THE DIVISION OF BIOCHEMISTRY, NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Synthesis of Calcium D,L-Glycerate-1-C^{14} [1]

BY H. J. SALLACH[2]

In order to study some of the metabolic reactions of glyceric acid in the animal organism, D,L-glyceric acid-1-C^{14} has been prepared as its calcium salt by the addition of HC^{14}N to hydroxyacetaldehyde followed by the hydrolysis of the resulting nitrile.

Glyceric acid, labeled with C^{14} in the carboxyl carbon, has been synthesized as its calcium salt by the addition of radioactive hydrogen cyanide to hydroxyacetaldehyde. The resulting nitrile was hydrolyzed without isolation. The reactions involved are shown below. The radioactive carbons are marked with an asterisk.



Experimental

Hydroxyacetaldehyde was prepared according to the procedure of Fischer and Taube.[3] For this purpose tartaric acid was converted into dihydroxymaleic acid by treatment at −5° with 30% hydrogen peroxide.[4] The resulting acid was then decarboxylated by heating in pyridine.

Sodium cyanide,[5] 98.7 mg., having a total activity of 750 microcuries, was diluted with 452.9 mg. of 95% non-labeled sodium cyanide. Hydrogen cyanide (10.7 millimoles) was then generated from the sodium cyanide in a vacuum line by the addition of 10 ml. of concentrated sulfuric acid. The liberated gas was collected by means of a liquid nitrogen trap in a reaction flask containing a trace of sodium cyanide as a catalyst. A solution of 700 mg. of hydroxyacetaldehyde (11.6 millimoles) in 4 ml. of water, which had been prepared 24 hours earlier, was added to this reaction vessel. The addition reaction was allowed to proceed at 0° for 30 minutes and then for an additional 30 minutes at room temperature. At the end of this time, 4 ml. of concentrated hydrochloric acid was added, and the nitrile was hydrolyzed for 30 minutes. The solution was then neutralized with calcium carbonate, boiled for 10 minutes with a slight excess of the calcium carbonate and filtered. The calcium salt of glyceric acid was then precipitated by the addition of four to five volumes of ethanol. The product was recrystallized by dissolving in a minimum amount of hot water, decolorizing with charcoal, and reprecipitating with ethanol. The yield of calcium glycerate, based on the sodium cyanide used, was 33%.

Anal. Calcd. for $(C_3H_5O_4)_2Ca \cdot 2H_2O$[6]: Ca, 13.99; C, 25.18; H, 4.93. Found: Ca,[7] 13.92; C, 25.16; H, 4.87.

The calcium glycerate had an activity of 141.7 microcuries per millimole or 70.9 microcuries per millimole of free glyceric acid. The activity of the diluted sodium cyanide used in the synthesis was 70.1 microcuries per millimole.

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