THE PREPARATION AND RESOLUTION OF dl-2-HYDROXY-3, 5-DINITROMANDELIC ACID*

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This acid has been prepared by cyanohydrin synthesis from 3,5-dinitrosalicylaldehyde. Salicylaldehyde was mixed with 5 parts of cold glacial acetic acid, and to this mixture 1.5 parts of fuming nitric acid were added slowly with cooling. The temperature was then allowed to rise to 45° C., when the solution was quickly mixed with 8 parts of cold water. A crystalline mixture of 3-nitro- and 5-nitro salicylaldehydes separated. This product was filtered off, washed with cold water, dried, and added cautiously to a nitrating mixture (1 part of concentrated nitric acid and 2 parts of concentrated sulfuric acid). The reaction mixture was kept below 10° C. for thirty minutes and then diluted with 3 volumes of cold water. The 3,5-dinitrosalicylaldehyde which separated was recrystallized twice from benzene. The recrystallized 3,5-dinitrosalicylaldehyde (M. P. 56° C.) was dissolved in 1.5 equivalents of hot 10 per cent sodium bisulfite solution. The solution was cooled and 1 equivalent of cold 20 per cent sodium cyanide solution was added slowly with stirring. After forty-five minutes the 2-hydroxy-3,5-dinitromandelonitrile was extracted with ethyl acetate. To this extract were added 2.5 gram-equivalents of concentrated hydrochloric acid; the ethyl acetate was removed by distillation, and the residue was heated on a boiling water bath for three hours. Twelve hours later the ammonium chloride was filtered off and the syrup was dissolved in a little water. Careful addition of saturated barium hydroxide solution produced yellow needles of barium *dl*-2-hydroxy-3,5-dinitromandelate. This barium salt, after recrystallization from boiling water, was found to contain 31.68 percent of barium (31.93 percent calculated for $BaC_8H_4O_8N_2.2H_2O$). The racemic salt was dissolved in 1 equivalent of N sulfuric acid and the solution was warmed with 4 volumes of ethyl alcohol. The barium sulfate was then removed by centrifuging and 1 equivalent of an alcoholic solution of brucine was added. Three fractions of brucine salt separated from the refrigerated mixture. After washing with alcohol and drying, the first and third fractions were found to contain 6.18 percent H and 55.29 percent C (6.20 percent H and 55.66 percent C calculated for $(C_{23}H_{26}N_2O_4)_2.C_8H_6O_8N_2.7H_2O$). These salts were suspended in water and converted to insoluble barium salts by the addition of 2 equivalents of saturated barium hydroxide solution. After recrystallization from hot water, the barium salts were converted to the free acids by addition of equivalent quantities of sulfuric acid solution. Filtered 1 per cent solutions of the acids were examined in the polariscope at 25° C., using an electric sodium lamp. The specific rotations of the acids from fractions 1 and 3 were found to be —33° and +41°, respectively. These antipodes of 2-hydroxy-3,5-dinitromandelic acid racemized rapidly in dilute sodium hydroxide solution and were therefore unsuited for incorporation into alkaline sugar reagents. To our knowledge they are the first optically active dinitrophenolic acids reported in the literature.

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* Contribution from the Department of Biochemistry, University of Oklahoma School of Medicine. Assisted by a grant from the Research Appropriation of the University of Oklahoma School of Medicine.