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-dinitro-
salicylaldehyde. 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 crystal-
line 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 con-
centrated 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 (31.92 percent calculated for BaC₃H₅O₃N₂·2H₂O). 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 56.29 percent C (6.20 per-
cent H and 55.66 percent C calculated for (C₁₃H₂₅N₁₂O₁₂)₂·C₃H₅O₃N₂·7H₂O). 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 unsuitable for incor-
poration into alkaline sugar reagents. To our knowledge they are the first
optically active dinitrophenolic acids reported in the literature.

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