Configuration of 2-Hydroxyputrescine

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SUMMARY

S-(+)-2-hydroxyputrescine·2HCl and R-(−)-2-hydroxyputrescine·2HCl were synthesized from S-(−)- and R-(+)-hydrosyputrescine·2HCl, respectively. Their specific rotations were determined to be \( [\alpha]^{20}_D = +3.21 \pm 0.06^\circ \) and \(-3.3^\circ\) (\( c = 5\% \), H₂O), respectively. The naturally occurring polyamine isolated from Pseudomonas (Kim) appears to be S-2-hydroxyputrescine since the specific rotation of its dihydrochloride corresponds closely to that of the synthesized S-(+)-2-hydroxyputrescine dihydrochloride.

We have previously shown that a pseudomonad which contains no spermidine (1) contains 2-hydroxyputrescine (2, 3). Derivatives of this polyamine have also been found in rust-resistant wheat leaves (4). Tobari and Tchen (5) have confirmed the presence of this polyamine in the pseudomonad and have reported its specific rotation to be +18.8°, but they have not determined its absolute configuration. Stoessl et al. (4) have assigned the chirality by a comparison of the melting ranges of 1:1 mixtures of the dihydrochlorides derived from natural sources with the synthetic materials of known configuration. The specific rotation of these “authentic specimens,” however, is reported as +7° and −7° for the S-(+) and R-(−) isomers, respectively.

Our own results agree qualitatively with these findings but differ markedly numerically. We have found a specific rotation \( [\alpha]^{25}_D \) of +3.2° for the dihydrochloride of the naturally occurring 2-hydroxyputrescine and +3.21 ± 0.06° (S.D.) for the S-(+)-2-hydroxyputrescine·2HCl which was synthesized from S-(+)-hydrosyputrescine·2HCl. The specific rotation of the corresponding R isomer was found to be −3.3° (\( c = 5\% \), H₂O).

The amides which were used as the starting materials for the synthetic amines were prepared from R- and S-malic acid according to published procedures and their purity was established by a comparison of their melting points and specific rotations with the values in the literature (6, 7). The reduction to the hydroxysuccinamide of 1,4-diaminobutanone (10), and with the dihydrochloride of the naturally occurring 2-hydroxyputrescine in melting point, magnitude of the specific rotation, paper electrophoretic mobility, and retention time on chromatographic columns.

Because of the discrepancy between the values which we obtained for the specific rotations and those which were observed by Tobari and Tchen (5) and Stoessl et al. (4), we have examined the concentration dependence of the specific rotation of the S isomer, since such a dependence, if existent, could very well account for the reported differences. We have found no recognizable trend of concentration dependence for aqueous solutions in the range from 0.5 to 15% (w/v). We have therefore calculated the mean value of the specific rotation \( [\alpha]^{25}_D = +3.21 ± 0.06^\circ \) (S.D.) from ten of our measurements.

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The melting ranges were determined on a Perkin-Elmer differential scanning calorimeter at a rate of heating of 2.5° per min. The first figure indicates the departure of the melting curve from the base-line, the second its maximum, and the third its return to the base-line.

The conditions for column chromatography and paper electrophoresis of 2-hydroxyputrescine have been described in Ref. 3. 1,4-Diaminobutanone was obtained from Aldrich Chemical Co., 2391 N. 30th Street, Milwaukee, Wis. 53210.
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