A New Imino Acid Derived from L-Serine *O*-Sulfate

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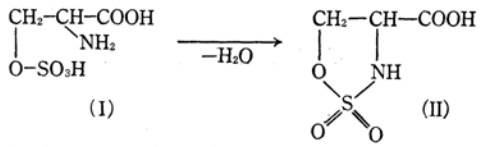
A new substance derived from L-serine *O*-sulfate was prepared chemically.



(I) (II)

L-Serine *O*-sulfate (I) was prepared in 40% yield from L-serine by the Dodgson's method.[1] L-Serine *O*-sulfate (500 mg) was dissolved in 5 m*l* of dimethylformamide (DMF), dicyclohexylcarbodiimide (500 mg) in 5 m*l* of DMF was added gradually to the solution with stirring at 0°C for 20 min. As the reaction proceeded, dicyclohexylurea was obtained. The reaction mixture was allowed to stand at room temperature for 3 hr. The precipitated dicyclohexylurea was filtered off and, after addition of 5 m*l* of water and 0.1 m*l* of glacial acetic acid, the white precipitates produced were separated by filtration, and the filtrate was evaporated to dryness in vacuo below 40°C. The oil like residue was dissolved in absolute alcohol, and the residue was separated by centrifugation, and then about four volumes of ether were added. After being kept in a refrigerator for 16 hr the precipitates were separated by centrifugation and the residue was dissolved in a few m*l* of water, then transfered to a column of Dowex 1 (X2) (100—200 mesh, Cl^- form, 15 cm×0.7 cm). The column was eluted with 0.1 N NH_4OH (30 m*l*), then eluted with 1 N HCl (20 m*l*). The eluate by 1 N HCl was concentrated *in vacuo* below 40°C. The oil like substance was dissolved in alcohol, and the residue was filtered off, and about two volumes of ether were added to the filtrate. The precipitate obtained was separated by centrifugation, and the residue was dissolved in a few milliliters of water and transferred to a column of Dowex 50 (X2) (50—100 mesh, H^+ form, 15 cm×0.7 cm). The column was washed with 30 m*l* of water and then the eluate and the washings were evapoated to dryness *in vacuo* below 40°C. The residue was dissolved in alcohol, and few milliliters of ether were added. The fine crystals were obtained. The yield was 70 mg. II is soluble in water, methyl alcohol and ethyl alcohol, insoluble in ethyl acetate, ether and petroleum ether. Melting point: 199—200°C (dec.). Found: C, 20.29; H, 4.20; N, 8.06%. Calcd for $C_3H_5O_5NS \cdot {}^1/_2H_2O$: C, 20.45; H, 3.41; N, 7.95%.

Paper chromatography was carried out on Toyo Roshi No. 50 paper by ascending solvent system; *n*-butanol : acetic acid : water, 4 : 1 : 2 (v/v); *n*-butanol : pyridine : water, 4 : 1 : 2 (v/v), *n*-propanol : aqueous ammonia (15 N) : water, 4 : 1 : 2 (v/v) were used as solvents. Spots were developed with ninhydrin. Color was red-purple. The R_f value of II was 0.16, 0.06 and 0.37 as a single spot respectively. The R_f value of I was 0.15, 0.03 and 0.42 respectively.

The infrared spectrum of II shows characteristic absorption bands in the 1210—1280 cm^{-1} and 800—810 cm^{-1} attributable to the S–O vibration and C–O–S vibration respectively. The C–O–S band of L-serine *O*-sulfate appears at 775 cm^{-1}.[2] Distinct difference was shown in the C–O–S frequency as mentioned above. Free COOH (1700 cm^{-1}) was strongly shown.

1) K. S. Dodgson, A. G. Lloyd and N. Tudball, *Biochem. J.*, **79**, 111 (1961).

2) A. G. Lloyd, N. Tudball and K. S. Dodgson, *Biochim. Biophys. Acta*, **52**, 413 (1961).