



the mixed copper salts in water and methanol. Regeneration of the parent acid from the less soluble copper salt gave DL-leucine (I), identified as its 3:5-dinitrobenzoyl-derivative and by its degradation with ninhydrin to isovaleraldehyde. Regeneration of the acid from the more soluble copper salt gave isoleucine (or alloisoleucine, II), identified by its degradation to methylethylacetaldehyde by means of ninhydrin. The compound $C_{12}H_{22}O_2N_2$ is therefore an optically active leucylisoleucine anhydride (III), deoxyaspergilline acid is either 2-hydroxy-3-isobutyl-6-sec-butylpyrazine (IV) or 2-hydroxy-3-sec-butyl-6-isobutylpyrazine (V), and aspergilline acid is either (VI) or (VII).

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¹ White, *Science*, **92**, 127 (1940). White and Hill, *J. Bact.*, **45**, 433 (1943).

² Dutcher, *J. Biol. Chem.*, **171**, 321, 341 (1947).

³ Newbold and Spring, *J. Chem. Soc.*, **373**, 1183 (1947). Baxter and Spring, *ibid.*, 1179 (1947).

Toxicity of Sulphydryl Compounds to Seeds

Audus and Quastel¹ have recently shown that sodium thiosulphate is toxic to seeds of higher plants, and it has been reported² that sodium ethyl xanthate is being used commercially as a weed-killer. The accompanying table shows the results of tests for toxicity to wheat seeds of a number of sulphydryl compounds, and may therefore be of interest.

| Group | Substance | Root fresh weight as per cent of control | | |
|-------|----------------------------------|--|--------|------------|
| | | Concentration | | |
| | | 0.0005M | 0.005M | 0.05M |
| A | thioacetic acid | 77 | — | — |
| .. | potassium thiocyanate | 96 | 79 | 27 |
| .. | sodium thiosulphate | 81 | 79 | 39 |
| .. | potassium dithio-oxalate | 95 | 90 | not tested |
| .. | potassium methyl dithiocarbonate | 50 | — | — |
| .. | potassium ethyl xanthate | 90 | 83 | — |
| B | n-propyl mercaptan | 101 | 97 | 82 |
| .. | i-propyl mercaptan | 95 | 104 | 90 |
| .. | ethyl mercaptan | 94 | 75 | 27 |
| .. | phenyl mercaptan | 80 | 38 | — |
| .. | cysteine hydrochloride | 110 | 45 | 16 |
| .. | thioglycolic acid | 81 | 45 | — |
| .. | o-thiolbenzoic acid | 89 | 81 | 51 |

Wheat seeds were sown on tap-water agar containing the toxic agents in Petri dishes and incubated

for four days at 24° C. The roots from each seed were then cut off and their fresh weight determined. Although most of the compounds tested showed some degree of toxicity, thioacetic acid and potassium methyl dithiocarbonate were outstanding in their toxicity; this has been confirmed in other experiments.

It has been suggested³⁻⁵ that the biological activity of ethylenic compounds is greatest where the substituent groups are electron-attracting. Walsh⁶ has commented on the similarity between —S— and —CH=CH—. We thought it possible, therefore, that the activity of sulphydryl compounds might be similarly explained. Ferric chloride gives colours with compounds of the type RSH and their salts. We have observed that the nature of the group R determines the colour. Groups, the phenyl derivatives of which give *meta* substitution when acted on by cationoid reagents, that is, groups which attract electrons, give red colours when their —SH compounds are treated with ferric chloride in water, ethanol or glacial acetic acid; the compounds listed in group A in the table fall into this category. RSH compounds with R-groups the phenyl derivatives of which give *ortho* or *para* substitution give green or blue colours with ferric chloride in water or alcohol and no colour in glacial acetic acid; those compounds listed in group B in the table fall into this category.

Though the most active two compounds, thioacetic acid and potassium methyl dithiocarbonate, fall into the group with R-substituents of high electron affinity, there is no general tendency for those compounds with R-substituents of high electron affinity to be more toxic than those with R-groups of low electron affinity. An explanation of the variation in toxicity among these sulphydryl compounds has, therefore, yet to be found.

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¹ Audus, L. J., and Quastel, J. H., *Nature*, **160**, 263 (1947).

² *Chem. and Eng. News*, **28**, 196 (1948).

³ Brian, P. W., Grove, J. F., and McGowan, J. C., *Nature*, **158**, 876 (1946).

⁴ McGowan, J. C., Brian, P. W., and Hemming, H. G., *Ann. App. Biol.*, **35**, 25 (1948).

⁵ Grove, J. F., *Ann. App. Biol.*, **35**, 37 (1948).

⁶ Walsh, A. D., *Quart. Rev. Chem. Soc. London*, **2**, (1), 73 (1948).