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CHEMICAL STUDIES ON LICHENS.

31.* A CYCLIC TETRAPEPTIDE FROM ROCCELLA CANARIENSIS.

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A cyclic tetrapeptide has been isolated from the lichen Roccella canariensis Darb. in 0.2 % yield. The compound is sparingly soluble in most organic solvents, insoluble in sodium hydroxide and slightly soluble in hydrochloric acid.

High resolution MS and elemental analyses established the molecular formula as $C_{28}H_{32}N_4O_4$, m.p. 320° (darkens, sinters at 285°), $[\alpha]_D^{25} = -92° \pm 2°$ (c=1, DMSO).

Acid hydrolysis yielded two compounds, separated by TLC and identified as L-prolin and d-β-amino-β-phenylpropionic acid (MS, $[\alpha]_D$, TLC).

Amino acid analysis showed the presence of two proline units in the compound. Besides, the empirical formula agrees with a residue of two β-amino-β-phenylpropionic acid units; the four amino acids being linked together as a cyclic peptide. Also the infrared absorption (KBr) at 3465, 3330, 1675, 1625 and 1520 cm^{-1} indicates amide linkages.

As the NMR spectrum indicates a symmetric compound, and excludes any other building blocks than prolin and β-amino-β-phenylpropionic acid, structure I seems to be the more probable for the peptide. Although this structure is also in keeping with biogenetic considerations, the alternative structure II cannot be completely ruled out.

The peptide is identical with the unknown compound reported from Roccella vicentina (1) and R. canariensis (2).

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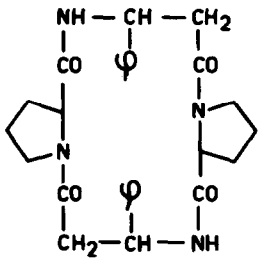
* Part 30. J. Santesson, Acta Chem. Scand., in press.



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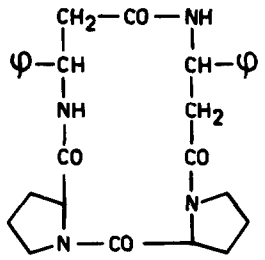

II

No oligo peptides have previously been isolated from lichens. A diketopiperazine derivative, picrococcellin, (3) has on one occasion (in 1877) been isolated from the lichen Roccella fuciformis (4).

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REFERENCES

1. S. Huneck and G. Follmann, Z. Naturforsch., 22b, 1369-1370 (1967).
2. S. Huneck, G. Follmann and H. Ullrich, Z. Naturforsch., 23b, 292-293 (1968)
3. M.O. Forster and W.B. Saville, J. Chem. Soc., 121, 816-827 (1922).
4. J. Stenhouse and C.E. Groves, Ann. Chem., 185, 14-25 (1877).