Trithiolaniacin, a Novel Trithiolan from Petiveria alliacea

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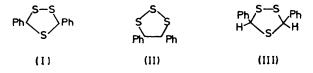
Summary Trithiolaniacin, a novel trithiolan characterized as cis-3,5-diphenyl-1,2,4-trithiolan was isolated along with sulphur, trans-stilbene, benzaldehyde, and benzoic acid from Petiveria alliacea.

THERE are few reports of systematic chemical studies of *Petiveria alliacea* L. (Phytolaccaceae). Rocha and Bonzani Da Silva reported the presence of nineteen coumarins in this species,¹ while Von Szczepanski *et al.* isolated a benzyl hydroxyethyl trisulphide from it.² We report the isolation of trithiolaniacin and other non-volatile components from the plant.

The chloroform extract of 1.5 kg of the wet root of P. alliacea collected at the end of the rainy season, was chromatographed on silica gel. Sulphur (0.05 g), trans-stilbene (0.25 g), benzaldehyde (0.81 g), and benzoic acid (0.24 g) were obtained,[†] together with a solid which separated out as white prisms (0.09 g), m.p. 92—95° from the hexane fraction. The solid trithiolaniacin, sublimed at 80°/0.05 mm, m.p. 93—94°, M^+ 276, analysed for C₁₄H₁₂S₃. The physical data (including n.m.r. and i.r.) suggest that trithiolaniacin is a diphenyltrithiolan with structure (I) or (II). The low-field position of the methine protons (δ 6.18) suggests structure (I) in which the hydrogen is adjacent to

+Confirmation of these known compounds was by i.r., n.m.r., m.p., mixed m.p. with the appropriate authentic specimens.

two sulphur atoms rather than (II).³ The m.s. resembles the fragmentation pattern of the corresponding ozonide,4 and 5,7-diphenyl-1,2,3,4,6-pentathiepan.⁵



No optical activity was detected for trithiolaniacin in chloroform, indicating either a cis- isomer or a racemate of the trans- form. An intense i.r. band at 725 cm^{-1} is evidence

¹ A. B. Rocha, and J. Bonzani Da Silva, Rev. Fac. Farm. Odontol. Araraquara, 1969, 3(1), 65 (Chem. Abs. 1970, 72, 397882).

¹ A. B. Rocha, and J. Bonzani Da Silva, Rev. Fac. Farm. Odontol. Araraquara, 1969, 3(1), 65 (Chem. Abs. 1970, 72, 39788z).
² Ch. Von Szczepanski, P. Zgorzelak, and G. A. Hoyer, Arzneim.-Forsch., 1972, 22(11), 1975 (Chem. Abs., 1973, 78, 5535h).
³ S. Fliszar, J. Carles, and J. Renard, J. Amer. Chem. Soc., 1968, 90, 1364; C. E. Bishop, D. D. Denson, and P. R. Story, Tetrahedron Letters, 1968, 55, 5789; A. M. Hamid and S. Trippett, J. Chem. Soc. (C), 1968, 1612; T. C. Shields and A. N. Kurtz, J. Amer. Chem. Soc., 1969, 91, 5415; S. B. Tjan, J. C. Haakman, C. J. Teunis, and H. G. Peer, Tetrahedron, 1972, 28, 3489.
⁴ J. Castonguay, M. Bertrand, J. Carles, S. Fliszar, and Y. Rousseau, Canad. J. Chem., 1969, 47, 919.
⁵ H. Tokunaga, K. Akiba, and N. Inamoto, Bull. Chem. Soc. Japan, 1972, 45, 506.
⁶ R. Crigee and G. Wenner, Annalen, 1949, 564, 9; R. Crigee and G. Lohaus, ibid., 1953, 583, 6.
⁷ G. Riezebos, J. C. Grimmelikhuysen, and D. A. Van Dorp, Rec. Trav. Chim., 1963, 82, 1234.
⁸ J. F. Carson and F. F. Wong, J. Agric. Food. Chem., 1961, 9, 140.

for the cis-stereochemistry, in line with Crigee's theory⁶ and the observation of Riezebos et al.7 The structure of trithiolaniacin is therefore proposed as cis-3,5-diphenyl-1,2,4trithiolan (III).

Aliphatic trisulphides have been isolated by Carson and Wong from onions (genus Allium).8

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