

Short Communications

Studies Related to Naturally Occurring Acetylene Compounds

XXXII. A Preliminary Note on a Red Acetylenic Pigment in *Eriophyllum caespitosum* Dougl.JULIUS THORVALD MORTENSEN,
JØRGINE STENE SØRENSEN and
NILS ANDREAS SØRENSEN*Institutt for Organisk Kjemi, Norges
Tekniske Høgskole, Trondheim, Norway*

In the chromatographic separation of naturally occurring acetylenic compounds coloured impurities often cause some difficulties. In our XXth communication of this series¹ we described *inter alia* one such pigment, $\lambda_{\max} = 4380 \text{ \AA}$, which although it was useful as it separated two acetylenes having very similar spectra, it was difficult to remove. The amount of this pigment has mainly been small and the purest fraction have showed such blurred visible light spectra that the purification of one of the pigments of this abundant type has been greatly hampered. Bohlmann, Kleine and Arndt² in a recent paper on a number of new thiophenic compounds in *Compositae* refer to similar experiences although their red pigments mainly absorb at longer wavelengths, $495 \text{ m}\mu$.

One pigment with a similar absorption has been observed in this laboratory from some *Eriophyllum* species $\lambda_{\max} = 5000 \text{ \AA}$. Ten years ago the crystallization of this pigment was achieved by one of the authors, (J.S.S.) but this usually helpful step did not prove to be so this time. The red dilute solutions are fairly stable. The ivory coloured crystals which may be obtained are mainly mixed crystals

with colourless polyacetylenes and the purer they are, the more rapidly is the pigment changed in the crystalline state into an insoluble polymer. In the pure state it cannot be stored as crystals more than 1/2 h at $+20^\circ\text{C}$.

These annoying properties have made it extremely difficult to get reliable analytical results and physical measurements not too much influenced by residual solvent.

An analysis for C and H (G. Cornali, Løvens Kemiske Fabrik, Copenhagen) fits the formula $\text{C}_{15}\text{H}_{12}\text{S}_2$ well; our micro sulphur values (S 25.3, 26.1), are in reasonable agreement with the same formula, calc. S 25.0. From what is stated above and general experience in the polyacetylene field the analytical results should be treated with reserve.

The IR-spectrum of I has a number of sharp bands, indicating the presence of $-\text{C}\equiv\text{C}-$ bonds (2237 (str.) , 2183 , 2150 cm^{-1}), a conjugated vinyl group (965 and 923 cm^{-1} , most likely $-\text{C}\equiv\text{C}-\text{H}=\text{CH}_2$) and a methyl group 1375 cm^{-1} . There is a strong band at 814 cm^{-1} so far displaced from the 800 cm^{-1} band of a 2,5-disubstituted thiophene that a highly polar substituent would be needed. Since the red pigment is eluted in the hydrocarbon fraction and no polar groups are revealed by IR such an explanation for this band is improbable. The side chains of substituted thiophenes are sometimes difficult to hydrogenate, and all efforts to reduce the red pigment to a thiophene derivative have failed. The reaction with Raney-nickel, however, is smooth and the main product is tridecane, a carbon skeleton identical with that of a large number of other polyacetylenes from the *Compositae*. With regard to the above mentioned analytical results the main problem appears to be whether 2 carbon atoms are split off during the reductive desulphurisation, or whether an analytical error of about 1.8 % in C

and 1.2 % in H may occur in a substance with such disagreeable properties.

A loss of 2 carbon atoms could be explained if the red pigment contained a vinyl sulphide (or disulphide) group. If the total number of carbon atoms is only 13 obviously a particular disposition of the sulphur atoms is needed to obtain a chromophore with a maximum at 5000 Å.

The red pigment reacts very easily in characteristic disulphide reactions, *e.g.* with potassium cyanide or sodium sulphite under the conditions given by Schöberl *et al.*,⁴ and in the zinchydroxyl-amine test according to Cheronis and Entrikin.⁵ As most of these reagents would also be expected to give reactions with a poly-acetylenic chain a check was carried out on dehydromatricaria ester to show that the acetylenic linkages were unchanged under conditions where the red pigment was quantitatively transformed. We have been unable to isolate the primary products from any of the disulphide reactions. They are very unstable and rearrange to short, indistinct chromophores.

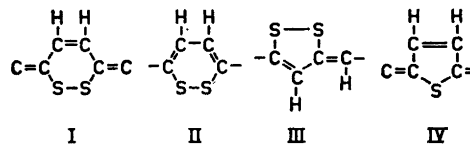
The NMR spectrum restricts the constitutional possibilities. Only eight protons seem to be present in the molecule. The characteristic multiplet of a vinyl group (3 H) is found between $\tau = 3.74$ and 4.48, which is apparently influenced by neighbouring protons, if at all. According to Drenth and Loewenstein⁶ ethynyl vinyl disulphide has the multiplet at 3.34–4.56 with a more pronounced chemical shift between the vinyl protons, caused by the deshielding effect of the sulphur atom on the proton next to it. In IR the vinyl sulphide group has the 10–11 μ bands at 965 and 860 cm^{-1} . The spectroscopic data thus exclude the possibility of the red pigment being a vinyl disulphide, which would have provided a ready explanation for the loss of 2 carbon atoms on reductive desulphurisation. Since there is good agreement with the literature data for $-\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2$, the position of the vinyl group may be restricted to this type or to a position on a conjugated ethylenic carbon atom devoid of hydrogen.

Three protons are found in a methyl singlet $\tau = 7.93$. The band is sharp and reveals no splitting when recorded at high resolution and slow sweep rate. According to model studies on poly-acetylenes in IR and NMR the possibilities may be restricted to either $\text{CH}_3-(\text{C}\equiv\text{C})_2\text{C}$

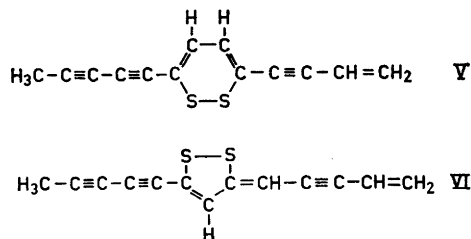
or $\text{CH}_3-(\text{C}\equiv\text{C})_3\text{C}$, with no hydrogen substituent on the other carbon atom attached to the acetylene chain.

The remaining two protons produce a quartet between $\tau = 3.34$ and 3.55. The coupling constant of approximately 6.5 cps is larger than that of any of the disubstituted thiophene isomers, and the chemical shift of the group is well outside the range of both acetylenic 2,5-disubstituted thiophene, as well as that of ethylenic protons in an aliphatic chain.

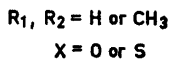
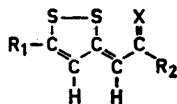
The deep red colour of a substance with only 13 carbon atoms in the chain necessitates the participation of the disulphide grouping in the chromophore. The 3 heterocycles I, II, and III should all be strong auxochromes.



III is part of the chromophore of the antibiotics thiolutin,⁷ aurothricin,⁸ and holomycin⁹ and is obviously a strong auxochromic group. The thiolene ring IV is also a strong chromophore.¹⁰ The corresponding disulphide grouping I, of which no representative seems to be known should be a stronger auxochrome than IV. I (and IV) would necessitate 4 olefinic protons instead of the observed 2 and so only the possibilities II and III remain:



V and VI thus should represent the most likely structures of the *Eriophyllum* pigment. Herz, Traverso and Walter¹¹ have studied the NMR spectra of some compounds of the general formula VII



VII

A direct comparison of these spectra with those obtained by us is not possible since different solvents have been used.

Under the conditions used by us the proton frequencies relative to tetramethylsilane should be τ 3.5–4. As no model studies have been carried out on type II disulphides no choice can be made between the formulae V and VI. As soon as further material becomes available the investigation will be continued with the aim of settling the problem of the structural formula.

1. Sørensen, J. S., Holme, D., Borlaug, E. T. and Sørensen, N. A. *Acta Chem. Scand.* **8** (1954) 1769.
2. Bohlmann, F., Kleine, K.-M. and Arndt, Chr. *Chem. Ber.* **97** (1964) 2125.
3. Schöberl, A. and Ludwig, E. *Ber.* **70** (1937) 1422.
4. Schöberl, A. and Krumej, F. *Ber.* **71** (1938) 2361.
5. Cheronis, N. D. and Entrikin, J. B. *Identification of Organic Compounds*, Interscience Publ. N. Y. — London 1963, p. 151.
6. Drenth, W. and Loewenstein, A. *Rec. Trav. Chim.* **81** (1962) 636.
7. Celmer, W. D., Tanner, F. W., Jr., Harfenist, M., Lees, T. M. and Solomons, I. A. *J. Am. Chem. Soc.* **74** (1952) 6304.
8. Celmer, W. D. and Solomons, I. A. *J. Am. Chem. Soc.* **77** (1955) 2861.
9. Ettliger, L., Gäumann, E., Hütler, R., Keller-Schierlein, W., Kradolfer, F., Neipp, L., Prelog, V. and Zähler, H. *Helv. Chim. Acta* **42** (1959) 563.
10. Jakobsen, H. J., Larsen, E. H. and Lawesson, S. O. *Tetrahedron* **19** (1963) 1867.
11. Herz, H. G., Traverso, G. and Waller, W. *Ann.* **625** (1959) 43.

Received October 8, 1964.

A $D8_s$ -Type Phase in the Yttrium-Tin System

SVEN HOLMÉN

Institute of Inorganic Chemistry, University of Stockholm, Stockholm, Sweden

The existence of intermediate phases at the compositions $Y\text{Sn}_{0.6}$ and $Y\text{Sn}_{1.6}$ in the yttrium-tin system has been reported by Terekhova *et al.*¹ No structural data about the phases were given.

In the present study, mixtures of yttrium (99.9%) and tin ("Baker's analyzed") were melted under helium (0.5 atm.) in an electric arc furnace. The samples were then annealed for 50 days at 850°C in evacuated sealed silica tubes. Tantalum foils protected the samples from reacting with the silica. The heat treatment was abruptly discontinued by quenching the capsules in cold water.

X-Ray powder patterns were registered in a Guinier focusing camera with $\text{CuK}\alpha$ radiation. The samples of compositions around $Y\text{Sn}_{0.6}$ gave patterns which could be indexed assuming a hexagonal unit cell with the dimensions

$$a = 8.902 \text{ \AA}, c = 6.536 \text{ \AA}, c/a = 0.734$$

These parameters are comparable with those of several $D8_s$ -type compounds of the formula A_3B_3 . Intensities calculated with atomic parameters of $Y_3\text{Sn}_3$ taken as $x_Y = 0.25$ and $x_{\text{Sn}} = 0.61$ were found to be in good agreement with the observed powder data. The $Y_3\text{Sn}_3$ phase seems to have a rather narrow homogeneity range. The phase is noticeably attacked by air even at room temperature. It is therefore not known so far if the material has a content of non-metal. Further studies on the Y-Sn system are in progress.

1. Terekhova, V. F., Markova, I. A. and Savitskii, E. M. *Zh. Neorgan. Khim.* **8** (1963) 1991.

Received November 16, 1964.