

Short Communications

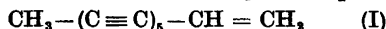
Studies Related to Naturally Occurring Acetylene Compounds

XXXI. A Preliminary Note on the Acetylenic Constituents of *Calocephalus citreus* Less.

JØRGINE STENE SØRENSEN, JULIUS THORVALD MORTENSEN and NILS ANDREAS SØRENSEN

Institutt for Organisk Kjemi, Norges Tekniske Høgskole, Trondheim, Norway

The trideca-pent-yn-ene (I) was originally isolated from some *Helipterum* spec.¹



Curiously enough this extremely unstable substance has turned out to have a very broad distribution within the family of the *Compositae*. Although its presence has been demonstrated in 10 out of the 13 tribes of the family,² its dominance seems to be most pronounced in the tribus *Inuleae* to which *Helipterum* belongs.

The Australian flora is supposed to have been isolated since early Cretaceous times from the rest of the world.³ Among the tribes of the *Compositae* the *Inuleae* has reached an astonishing development on the Australian continent.

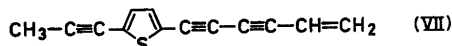
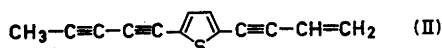
In connection with a rather broad investigation of the polyacetylenes of Australian *Compositae*, made possible by extensive assistance from the Organic Chemistry Division of the C.S.I.R.O., Melbourne, we also have investigated available members of the tribus *Inuleae* for the presence of (I). This pent-yne was found to be as characteristic of Australian genera of this tribus as earlier investigations had shown it to be of genera of the Old World with one single exception, *viz.* *Calocephalus citreus* Less.

Although the lipids of all part of this plant was investigated by careful chromatography no trace of (I) could be discovered. The main acetylenic constituents of *C. citreus* are two new thiophenic compounds, a hydrocarbon (II), and a free acid, (III).

(II) is a rather difficult compound to crystallize, m.p. 5–10°C. The sulphur content 16.2% corresponds to $\text{C}_{13}\text{H}_8\text{S}$, calc. 16.35. IR disclosed by a strong band at 800 cm^{-1} that the sulphur is present in a 2,5-disubstituted thiophene ring. Else IR definitely indicated disubstituted acetylenic bonds, bands at 2247, 2198 and 2155 cm^{-1} , a vinyl group, but no further double bonds, and a methyl group. Reductive desulphuration gave tridecane, whereas partial hydrogenation furnished a liquid 2,5-dialkylthiophene whose structure we attempted to prove by synthesis of the three possible isomers: 2-methyl-5-octyl (IV), 2-propyl-5-hexyl (V) and 2-butyl-5-pentyl thiophene (VI). (IV) could easily be distinguished from the hydrogenation product of (II) by gas chromatography. Otherwise the corresponding acetylenic thiophene with the entire unsaturation on one side should be expected to give a pronounced fine structure spectrum in UV in contrast to (II). The two other substances (V) and (VI) could not be distinguished by gas chromatography neither from each other, nor from the partial hydrogenation product from (II). Earlier work in the pristane series indicated that these two isomers should differ in their IR-spectra in the 13–14 μ region. (VI) showed absorption at 728 cm^{-1} characteristic of a $-(\text{CH}_2)_4-$ chain, as compared with 727 cm^{-1} *cf.* Ref.⁴ In this region (VI) differs characteristically from (IV) and (V) but coincides with tetradecahydro- (II), thus establishing the carbon skeleton of (II).

In UV (II) has one broad band with blurred fine-structure with a first maximum at 3570 Å and weak bands at 3400 and 3300 Å. (II) thus must be fully conjugated.

NMR confirmed the presence of 3 H in a vinyl group, 2 H in the 3:4 position of a thiophene ring and placed the remaining 3 hydrogens in a methyl group. The combined evidence points to 2-[pent-1,3-diynyl]-5-[but-1-yn-3-enyl]-thiophene (II).



Bohlmann, Kleine and Arndt² recently isolated a liquid acetylenic thiophene from *Schkuhria senecioides* Ness. for which their primary evidence left the choice between (II) and (VII). (VII) was chosen on the basis of the result of the mass spectrometric analysis of the hydrogenation product. As compared by their physical data, the hydrocarbons from *Calocephalus* and *Schkuhria* look very similar.

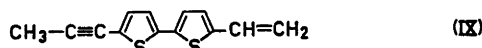
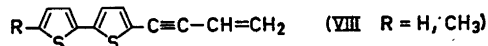
Formula (II) is further supported by two additional spectroscopic points. Thiophene derivatives containing the α -propargyl group in the 2-positions either show no noticeable absorption in the methyl region at 7.25μ or a band of only abnormally low intensity. Acetylenic compounds with the grouping $\text{CH}_3-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$ do show a band of the usual intensity.

In the NMR spectrum the methyl group of (II) is found at $\tau = 8.00$, in excellent agreement with the data given in literature for 1,3-pentadiyne residues, $7.99-8.03$.^{5,6} For methyl groups in the prop-yn substituent, however, the position is shifted to 7.83 . Both these facts support (II). According to Bohlmann *et al.*² the *Schkuhria* hydrocarbon has the methyl peak at $\tau = 7.92$.

The *Calocephalus*-hydrocarbon (II) adds on H_2S under the specific conditions elaborated by Schulte *et al.*⁷ The bithienyl-compound formed (VIII, R = CH_3) had m.p. $46=47^\circ\text{C}$ and showed UV-absorption very close to that of 5-[buten-(3)-yn-

(1)-yl]-2:2'-bithienyl (VIII, R = H), the nematocidal principle of *Tagetes spec.*⁸

These thiophene derivatives (VIII) are rather remarkable by the fact that their first UV-maximum is some 200 \AA shorter than expected. In accordance with structure (VIII, R = CH_3) the vinyl bands in the $10-11 \mu$ range are at 965 and 914 cm^{-1} , characteristic of the grouping $-\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2$.⁹



The *Schkuhria*-formula (VII) would give the dithienyl-derivative (IX) where the vinyl bands would be at 980 and 900 cm^{-1} .

Details of this work will be published in the Australian Journal of Chemistry.

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. Burbidge, N. T. "The Phytogeography of the Australian Region", *Australian Journal of Botany* **8** (1960) 75.
4. Plíva, J. and Sørensen, N. A. *Acta Chem. Scand.* **4** (1950) 846.
5. Bohlmann, F., Bornowski, H. and Arndt, Chr. *Ann.* **668** (1963) 53.
6. Bohlmann, F., Arndt, Chr., Bornowski, H., Kleine, K.-M. and Herbst, P. *Chem. Ber.* **97** (1964) 1179.
7. Schulte, K. E., Reisch, J. and Hörner, L. *Chem. Ber.* **95** (1962) 1943.
8. Uhlenbrock, J. K. and Bijloo, J. D. *Rec. Trav. Chim.* **77** (1958) 1004; **78** (1959) 382; cf. Bohlmann, F. and Herbst, P. *Chem. Ber.* **95** (1962) 2945.

Received September 22, 1964.