Studies Related to Naturally Occurring Acetylene Compounds XXIV. 2-Phenyl-5(α-propynyl)-thiophene from the essential oils of Coreopsis grandiflora, Hogg ex Sweet

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A crystalline compound, m. p. 43°, isolated from the flowers and leaves of Coreopsis grandiflora, Hogg ex Sweet, has been shown to be 2-phenyl-5-(α-propynyl)-thiophene (III) by synthesis of the tetrahydro compound 2-phenyl-5-n-propyl-thiophene. The relation of (III) and other naturally occurring thiophenes to polyacetylenic compounds is discussed.

The preceding (XXIIIrd) communication of this series described the isolation of 1-phenylheptatriyne (I) from some perennial members of the genus Coreopsis1. (I) was the dominating chromophore of all parts of these oils and in some cases (I) crystallised directly from the crude oils. The oils from all parts of the plants were, however, fractionated by chromatography on slightly deactivated alumina in the usual way. (I) then appeared with the eluates with 10 % benzene in petroleum ether. Since Coreopsis species mostly have been characterised by a mixture of polyenic hydrocarbons, the eluates with 10 % benzene in petroleum were arbitrarily divided into a number of fractions. After evaporation of these solutions in vacuum pure (I) crystallised immediately.

\[ \text{(I)} \quad \text{C}_5\text{H}_8 \quad \text{C} \equiv \text{C} \quad \text{C} \equiv \text{C} \quad \text{C} \equiv \text{C} \quad \text{CH}_3 \]

\[ \text{(II)} \quad \text{CH}_3 \quad \text{C} \equiv \text{C} \quad \text{C} \equiv \text{C} \quad \text{C} \equiv \text{C} \quad \text{CH}_3 \]

When this standard procedure was applied to the extract from Coreopsis grandiflora, Hogg ex Sweet, five nice looking crystallisates were obtained, to the naked eye apparently very similar. The three first fractions melted sharply
around 54°C, the two later also rather sharply, but around 40°C. Recrystallisation brought the m.p. of the later to 43°C.

The U.V.-Spectrum, Fig. 1, curve A, with the broad single maximum at 3 100 Å did not indicate any relationship to phenylheptatriyne-1. The infrared spectrum, Fig. 2, curve A, with the sharp peak at 2 240 cm⁻¹ revealed that the new compound was a disubstituted acetylene, further the characteristic peaks at 688 and 753 cm⁻¹ indicated a monosubstituted phenyl residue.

Catalytical hydrogenation gave a liquid hydrocompound with a consumption of hydrogen so small that on a reasonable molecular weight obviously only the acetylenic bond had been hydrogenated. This was confirmed by the infrared spectrum of the tetrahydrocompound where the acetylenic band had disappeared, Fig. 2, curve B. The U.V.-spectrum of the tetrahydro compound, Fig. 1, curve B, demonstrated on one hand by the movement of the maximum about 200 Å towards shorter wavelengths relative to the starting material that the acetylenic bond was conjugated with the main chromophore, on the other hand that the tetrahydro compound must contain another chromophore resistant towards hydrogenation and conjugated with the phenyl group. Since carbonyl groups were absent, this result was somewhat surprising. Just at this stage of the investigations, however, appeared the communication of Birkinshaw and Chaplen¹ about one of the volatile components, "Junipal", of Daedelia juniperina, for which they proved the constitution 6-(α-propynyl)-

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Fig. 2. Infrared absorption of

A. 2-phenyl-5-(α-propynyl)-thiophene (III) in CS$_2$; $c = 24 \%$; $l = 0.05$ mm; dotted curve in CCl$_4$.
B. 2-phenyl-5-n-propyl thiophene liq.
C. 2-phenyl-thiophene liq. $l = 0.0125$ mm.
D. 2-phenyl-5-propionyl-thiophene in CS$_2$, $c = 9.6 \%$; $l = 0.05$ mm.

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2-formyl-thiophene (II). As there were some similarities in the infrared spectra of the new compound, m.p. 43°, was analysed on sulphur and gave 16.0 % S, calc. for C_{15}H_{10}S: S 16.3.

A compilation of the known infrared spectra of thiophenes, surveyed in the following communication, revealed that 2,5-disubstituted thiophenes are characterised by a single, strong peak at about 12.5 μ whereas all the other types of substituted thiophenes have two or more bands in other positions in the 11—15 μ area.

As will be seen from Fig. 2 the new compound fits well into the 2,5-disubstituted class and the observations cited then definitely pointed to the constitution as 2-phenyl-5-(α-propynyl)-thiophene (III).

The easiest way to prove this conclusion was by synthesis of the tetrahydro compound, 2-phenyl-5-n-propylthiophene, which followed the route 2-phenylthiophene → 2-phenyl-5-propionylthiophene → 2-phenyl-5-n-propylthiophene which, as expected, turned out to be identical in the U.V. and infrared with the tetrahydro compound.

The new compound, m.p. 43, so definitely was proved to be 2-phenyl-5-(α-propynyl)-thiophene. Only 2 thiophene derivatives so far have been considered as naturally occurring thiophenes. The origin of the very numerous thiophene derivatives isolated from petroleum or shale oils is still quite uncertain. The first to be found was terthienyl (IV) isolated by Zechmeister and Sease from the petals of the so-called "African" variety of Tagetes erecta L., belonging to the family of the Compositae, Tribus Heliantheae. The second was the above mentioned "Junipal" (II) from Daedelia juniperina, a bassidiomycete. Challenger and Holmes suggested a connection between the occurrence of terthienyl and various polyacetylenes in the Compositae. Such a connection could be a very close one between 1-phenylheptatriyne (I) and 2-phenyl-5-(α-propynyl)-thiophene (III), as only an addition of hydrogen sulphide to a di-acetylenic group would transform (I) into (III) — chemically not at all an unlikely reaction. Terthienyl, which recently has been found in another Compositae plant, Echinops sphaerocephalus, would, however, by such a process demand the acetylenic precursor hexa-acetylene V

\[
\text{V) H} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}
\]

\[
\begin{align*}
\text{VI) } \text{HOOC} & \equiv \text{C} \equiv \text{C} \equiv \text{C} & \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH} \\
& \equiv \text{O} & \equiv \text{O} & \equiv \text{O} & \equiv \text{O} & \equiv \text{O}
\end{align*}
\]

As is well known the stability of unsubstituted acetylenes decreases very rapidly with chain-length. Diacetylene may be distilled, b.p. 9.5—10°, triacetylene decomposes already at —50°; efforts to synthesise higher free polyacetylenes have only led to carbonaceous material. Thus even in dilute solution in plant cells in the presence of possible stabilisers the occurrence of hexa-acetylene itself sounds very unlikely. We think it is more probable that some poly-keto precursors analogous to the poly-β-keto-precursors originally proposed by Collie and revived in recent years by Robinson, Birch, Lipmann and Woodward, may be the common precursors to both polyacetylenes and naturally occurring thiophenes. A direct formation of the

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thiophene nucleus demands 1:4-diketo groupings, for example VI. It may be, however, that the ordinary β-keto-scheme is at work, that however, dehydration and thiophene formation follow stepwise:

\[
\begin{align*}
\text{CH}_3&-\text{CO}-\text{CH}_3&-\text{CO}-\text{CH}_3&-\text{CO}-\text{CH}_3&-\text{CO}-\text{CH}_3&-\text{CO}-\text{COOH} \\
\text{HC}&\equiv\text{C}&-\text{C}&-\text{CH}_3&-\text{CO}-\text{CH}_3&-\text{CO}-\text{CH}_3&-\text{CO}-\text{CH}_3&-\text{CO}-\text{COOH} \\
\text{C}&\equiv\text{C}&-\text{C}&-\text{C}&-\text{CH}_3&-\text{CO}-\text{CH}_3&-\text{CO}-\text{COOH} \\
\text{C}&\equiv\text{C}&-\text{C}&-\text{C}&-\text{C}&-\text{COOH} \\
\text{IV} \\
\text{C}&\equiv&\text{C}&\equiv&\text{C}&\equiv&\text{C}&\equiv&\text{C}&\equiv&\text{C}&\equiv&\text{C}&\equiv&\text{C} \\
+ \text{ CO}_2
\end{align*}
\]

We hope to bring further information on this interesting problem as preliminary investigations have revealed that about a dozen new compounds from members of the Compositae are really thiophene derivatives, in part acetylenic thiophenes.

The above mentioned Echinops sphaerocephalus is a very interesting case since it contains both terthiophenyl (IV) and some new polycyctenes. The content of acetylenic compounds is low which makes progress rather difficult.

That the connection formally is in some cases as close as between phenyl-heptatriyne (I) and 2-phenyl-5-(α-propynyl) thiophene (III) has been demonstrated by a new compound isolated by E. Guddal from Chrysanthemum vulgare and for which he so far has been able to restrict the constitutional possibilities to (VII) and (VIII) which, however, formally are generated from the dehydro- aromatichic amused ester (IX) — found in closely related species — by addition of H₂S.

\[
\begin{align*}
\text{CH}_3&-\text{C}&\equiv&\text{C}&-\text{C}&\equiv&\text{C}&-\text{C}&-\text{C}&-\text{C}&-\text{CH} = \text{CH} & \text{COOCH}_3 \\
\text{CH}_3&-\text{C}&\equiv&\text{C} \\
\text{CH} = \text{CH} & \text{COOCH}_3 \\
\text{CH}_3&-\text{C}&\equiv&\text{C} & \text{CH} = \text{CH} & \text{COOCH}_3
\end{align*}
\]

**EXPERIMENTAL**

The Coreopsis grandiflora oils used in this investigation are the same as in the preceding communication. III was not found in the extract from the root; the behaviour of the essential oils from the leaves and the flowers was so similar that only one of them is reported. Ca. 4 g of essential oil from the leaves (no accurate weight is given as the evaporation of the solvent (petroleum ether) intentionally was somewhat incomplete) was chromatographed on deactivated alumina. The material in the fractions containing 4–8 % benzene in petroleum ether crystallised immediately, all gave the correct m. p. 54–55° and had the characteristic ultraviolet spectrum of phenyl-heptatriyne (I). The succeeding eluates containing 8–15 % benzene in petroleum ether also crystallised very

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well on evaporation to give prismatic needles resembling those of (I) very much, the m. p., however, was in the 40° range. Admixture with (I) gave a liquid at room temperature. Recrystallisation gave a sharp m. p. 42—43°. (Found (Zimmermann): S 15.4 and 16.0. Calc. for C_{12}H_{20}S: S 16.3.) Ultraviolet spectrum in hexane, Fig. 1, curve A; log ε_{max} = 4.43; λ_{max} = 3 100 Å; infrared spectrum, Fig. 2, curve A.

Catalytic hydrogenation. 27.7 mg (III) was hydrogenated with a Pd—BaSO₄ catalyst in alcohol. Consumed 6.9 ml hydrogen, t = 18.5°C, p = 758, calculated for C_{12}H_{20}S, I = 6.95 ml. The tetrahydro compound was isolated in the usual way and distilled, b. p. 45° (air bath) at 0.001 mm Hg. Ultraviolet spectrum of the tetrahydro compound in hexane, Fig. 1, curve B; log ε_{max} = 4.30; λ_{max} = 2 900 Å. Infrared spectrum of the tetrahydro compound, Fig. 2, curve C.

Synthesis of 2-phenyl-5-n-propylthiophene. 2-Phenyl-thiophene was synthesised from β-benzoylpropionic acid according to Chrzasz-Czewska. The m. p. of 2-phenylthiophene could not be raised above 32—33°C; reported 42—43°. (Found: S 19.8 and 19.5. Calc. for C_{12}H_{20}S: S 20.0.) Infrared spectrum Fig. 2, curve C.

650 mg of 2-phenylthiophene was condensed with 1 g of propionyl chloride according to Hartough and Kosak. The reaction mixture was diluted with ether and then washed with water, potassium hydroxyde, water and the solvent was evaporated. The residue was distilled in high vacuum giving 360 mg of distillate which partly crystallised. Recrystallisation from petroleum ether gave slightly coloured plates, m. p. 87—88°. (Found: S 14.8. Calc. for C_{12}H_{18}SO: S 14.75.) Infrared spectrum of 2-phenyl-5-propionylthiophene, Fig. 2, curve D. A Clemmensen reduction of 2-phenyl-5-propionylthiophene was first attempted in water at room temperature according to Fieser and Kenelly. About one half of the unchanged ketone was recovered, the rest was lost. Then 100 mg of 2-phenyl-5-propionylthiophene was reduced with 2 g of amalgamated zink in alcoholic solution (6 ml of ethanol, 4 ml of hydrocyan chloride (1:1)). The solution became turbid but turned clear with stirring and slight warming, reaction time 2 h.

The crude reaction product was devoid of carboxyl bands in the infrared. The oil was distilled, b. range 60—65°, air bath, 0.001 mm Hg. Ultraviolet and infrared spectra of the distillate were identical with those of the tetrahydro compound, thus is 2-phenyl-5-n-propylthiophene.

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REFERENCES


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