

**Studies Related to Naturally Occurring Acetylene
Compounds. Part XXV. The Occurrence of Methyl
cis- β (5-Propynyl-2-thienyl)-acrylate in the Roots of Tansy**

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The roots of tansy (*Chrysanthemum vulgare* Bernh.) have been investigated for their content of acetylenic compounds, and a sulphur containing compound identified as methyl *cis*- β (5-propynyl-2-thienyl)-acrylate has been isolated.

As briefly mentioned previously¹, the investigation of the highly unsaturated compounds in the roots of *Chrysanthemum vulgare* Bernh. has revealed the presence of an ester of a sulphur containing C₁₀-carboxylic acid. This compound is present in approximately the same amounts in acetone extracts and in the volatile oil obtained by steam distillation of the roots. The isolation, however, is best achieved by the latter method. From the oil of roots collected in the autumn or the late summer, the unsaturated ester crystallized on cooling to -10°C. This would indicate a certain increase in the content of this compound during the summer season, accompanied by distinctly increasing amounts of volatile oil during the same period. (Calculated on fresh roots, the yields of volatile oil range from 160 p.p.m. in June to 250 p.p.m. in August.)

When chromatographed on deactivated alumina, the unsaturated ester was eluted with light petroleum-benzene (2:1), and crystallized in nearly colourless prisms from hexane. It showed a melting point of 101°C in an evacuated tube, and elementary analysis agreed with C₁₁H₁₀O₂S. Its infrared spectrum is shown in Fig. 1 A. The infrared absorption bands at 1 435 cm⁻¹ and 800 cm⁻¹ indicate that the sulphur atom is present in a thiophene nucleus², and the band at 2 220 cm⁻¹ shows the presence of a triple bond. A strong band at 1 715 cm⁻¹ followed by another strong band at 1 618 cm⁻¹ indicates an α,β -unsaturated carbonyl group. The very strong band in the ethylenic stretching region and the very moderate absorption in the acetylenic stretching region makes it probable that the double bond and not the triple bond is conjugated with the carbonyl group³.

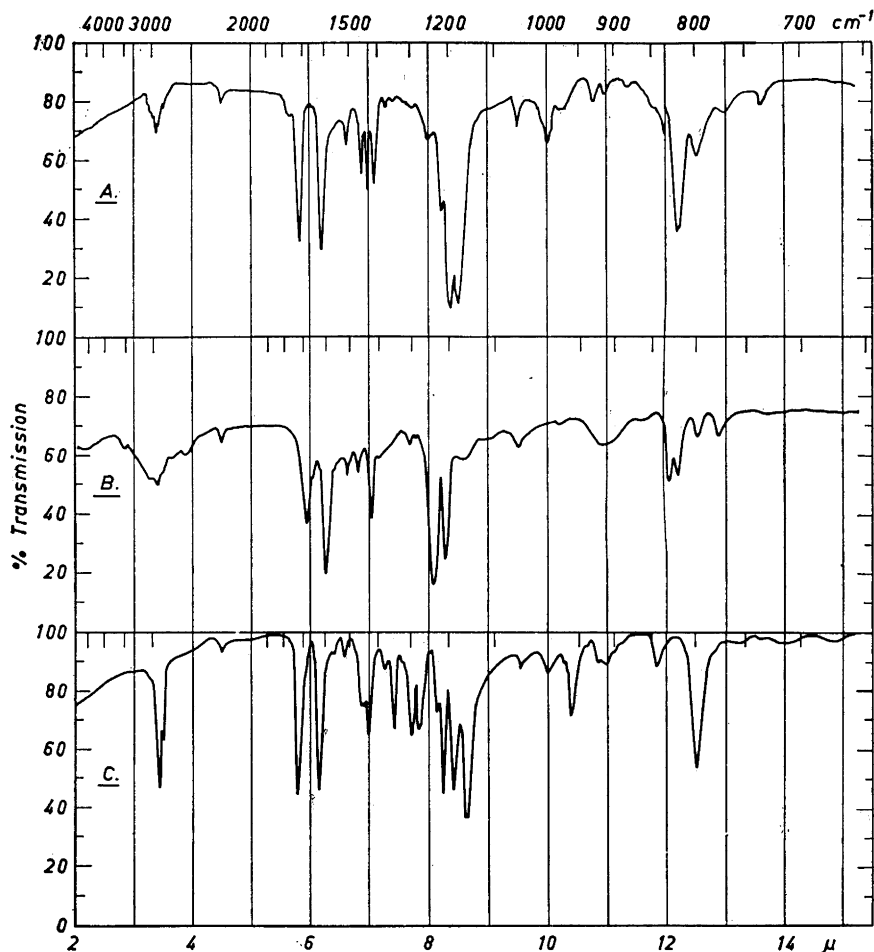
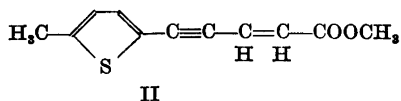
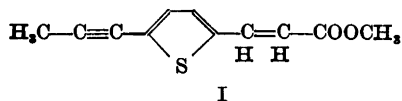


Fig. 1. Curve A: Methyl-*cis*- β (5-propynyl-2-thienyl)-acrylate. In CHCl_3 , 2–12 μ , in CS_2 , 12–15 μ . Curve B: *Cis*- β (5-propynyl-2-thienyl)-acrylic acid. In KBr-disc. Curve C: Methyl-*trans*- β (5-propynyl-2-thienyl)-acrylate. In KBr-disc.

Hydrolysis under mild conditions gave an acid in poor yield which after recrystallisation from ether-hexane, was obtained as yellow needles melting at 148.5–149.5°C (decomp.), and the oxygen atoms thus obviously belongs to an ester grouping. The infrared spectrum of this acid is shown in Fig. 1 B.

The data leave only the two constitutional formulas I and II as reasonable structures.



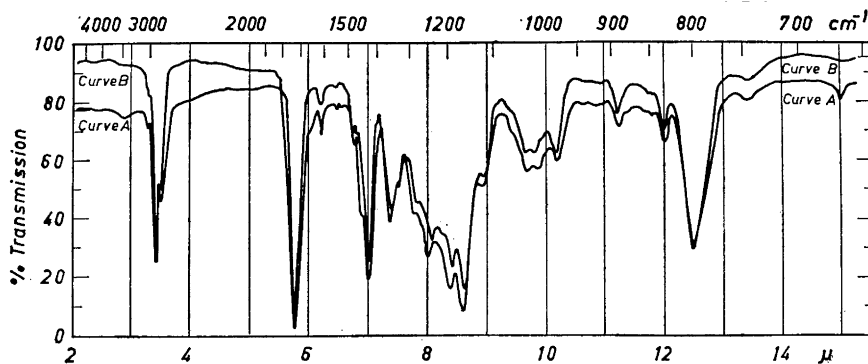


Fig. 2. Curve A: Hexahydro-methyl- β (5-propynyl-2-thienyl)-acrylate. Liq. Curve B: Synthetic Methyl- β (5-propyl-2-thienyl)-propionate. Liq.

The choice between I and II was made possible through a study of the hexahydro-compound. Catalytic hydrogenation of the unsaturated ester on Pd/BaSO_4 gave nearly colourless oil with a pleasant, sweetish odour, identical with synthetic methyl β (5-propyl-2-thienyl)-propionate, as shown by the identity of their infrared spectra which are reproduced in Fig. 2. The acid obtained upon saponification of this ester showed an infrared spectrum identical with that of synthetic β (5-propyl-2-thienyl)-propionic acid, and its melting point was not depressed on admixture of this compound. The synthetic specimens for these comparisons are readily obtained by hydrogenation of β (5-propyl-2-thienyl)-acrylic acid⁴ with sodium amalgam according to Barger and Easson⁵, and subsequent esterification of the acid. It thus follows that the new compound is methyl β (5-propynyl-2-thienyl)-acrylate (I).

When irradiated in the presence of iodine, the natural, unsaturated ester was partly converted to the *trans*-isomer which melted at 76°C and crystallized from hexane in thin leaflets. Its infrared spectrum, as shown in Fig. 1 C, contains a strong absorption band at 960 cm^{-1} , indicative of a *trans*-double bond. The *cis*-configuration of the natural ester could not conclusively be stated from its infrared spectrum because the *cis*-absorption band appeared at 820 cm^{-1} , very close to the band at 800 cm^{-1} characteristic of 2:5-disubstituted thiophenes². Based on this evidence we conclude that the structure of the natural, unsaturated ester is methyl *cis*- β (5-propynyl-2-thienyl)-acrylate (I).

Varying amounts of the *trans*-isomer have also been isolated from the plant material. An acetone extract worked up in the dark, however, contained only traces of this isomer, and it is most probably an artefact.

Methyl *trans*- β (5-propynyl-2-thienyl)-acrylate has recently been synthesized in this laboratory⁶ and proved identical with the *trans*-isomer of the natural compound.

EXPERIMENTAL

Nine kg of fresh roots of *Chrysanthemum vulgare* Bernh. collected in August were steam distilled to give a yellowish brown volatile oil. On prolonged cooling at -10°C , slightly yellow prisms were deposited. The supernatant oil was submitted to chromatography on

deactivated alumina. The fraction eluted with light petroleum-benzene (2:1) afforded additional amounts of this crystalline compound. After two crystallisations from hexane, the compound melted at 101°C in an evacuated capillary. On heating in air, the compound showed destruction at 50–60°C, and was completely carbonized before melting occurred. The yield of this compound was 90 mg. (Found: C 63.5; H 5.05; S 15.1–15.4. Calc. for $C_{11}H_{10}O_2S$: C 64.0; H 4.88; S 15.5.) The ultraviolet spectrum has two broad maxima at 3 415 Å (log ϵ : 3.85) and 2 350 Å (log ϵ : 3.57). Infrared spectrum Fig. 1, curve A.

Saponification. 10 mg of the isolated compound was treated for one hour at room temperature with 5 % KOH in dilute EtOH (water : EtOH 2:1). From the reaction mixture 2 mg of an acidic compound was obtained. It crystallized from an ether-hexane mixture in beautiful, yellow needles, melting with destruction at 148.5–149.5°C. (Found: S 16.26. Calc. for $C_{10}H_8O_2S$: S 16.6.) The ultraviolet spectrum in hexane shows one maximum at 3 260 Å (log ϵ : 3.75). Infrared spectrum Fig. 1, curve B.

Hydrogenation. 26 mg of the isolated compound was hydrogenated with a 5 % Pd/BaSO₄ catalyst in ethanol solution. 8.6 ml hydrogen was consumed (755 mm Hg, 20°C), corresponding to 3.1 double bonds at a molecular weight of 206. The hydrogenation product was a nearly colourless oil with a pleasant, sweetish odour. It distilled at 40–45°C (bath temperature) at 3×10^{-3} mm Hg. n_D^{20} 1.5043. Infrared spectrum Fig. 2, curve A.

14 mg of the distilled hydrogenation product was saponified as above, and an acidic substance, which crystallized from hexane in ill-defined prisms, was isolated. It was obtained pure after distillation at 80–85°C (bath temperature) at 5×10^{-5} mm Hg, and subsequent crystallisation from hexane. The best preparation melted at 57–58°C, not depressed on admixture with synthetic β (5-propyl-2-thienyl)-propionic acid.

Isomerisation. To a solution of 10 mg of the natural, unsaturated ester in hexane was added a small amount of iodine, and the solution was irradiated with a mercury lamp for 45 min. Chromatography on deactivated alumina of the reaction mixture furnished 4 mg of unchanged material, and 4 mg of a new compound, eluted from the column with benzene-light petroleum (2:1). It crystallized from hexane in thin leaflets, melting at 76°C. Varying amounts of this compound also could be isolated from the volatile oil, the identity being proved by identical infrared spectra and mixed melting point determination. Its ultraviolet spectrum shows two broad maxima at 3 370 Å (log ϵ : 4.43) and 2 300 Å (log ϵ : 3.95). Infrared spectrum Fig. 1, curve C.

Preparation of β (5-propyl-2-thienyl)-propionic acid and its methyl ester. β (5-propyl-2-thienyl)-acrylic acid ⁴ was dissolved in saturated sodium bicarbonate solution and shaken with excess 3 % sodium amalgam at 10°C. Throughout the reaction, carbon dioxide was bubbled through the solution to avoid excessive rise in pH. After acidification, the acid obtained was taken up in ether and recrystallized from ether-hexane. M. p. 59.5–60°C. Yield 90 %. The acid was esterified by boiling with methanol and H₂SO₄, and the ester was distilled at 35–40°C (bath temperature) at 10^{-3} mm Hg. Yield 62 %. Infrared spectrum Fig. 2, curve B.

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