

Studies Related to Naturally Occurring Acetylene Compounds

XXIX. Preliminary Investigations in the Genus *Bidens*: I. *Bidens radiata* Thuill and *Bidens ferulaefolia* (Jacq.) DC.

SYNNÖVE LIAAEN JENSEN and NILS ANDREAS SÖRENSEN

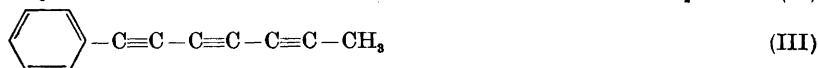
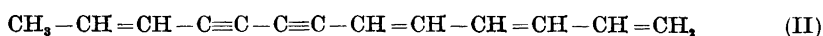
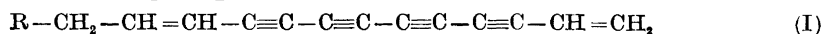
Institutt for Organisk Kjemi, Norges Tekniske Högskole, Trondheim, Norway

A preliminary investigation of 2 species of the genus *Bidens*, viz. *B. radiata* Thuill and *B. ferulaefolia* (Jacq.) DC. has revealed the occurrence of a number of the polyacetylenes previously isolated from several members of the genus *Coreopsis*. The diene-tetrayne I was found both in the nonpolar form I, R = H, and as a polar derivative supposed to be I, R = OCOCH₃. Further the trideca-1,3,5,11-tetraene-7,9-diyne II could be isolated in crystalline form. The presence of 1-phenylhepta-1,3,5-triyne could be demonstrated only spectroscopically. *B. radiata* furnished two fractions containing substances with broad absorption bands in the ultraviolet. One of them could be obtained pure, and preliminary constitutional work indicated the structure IV = 5-methyl-5'-buta-1,3-dienyl-2,2'-dithienyl.

Among the numerous genera of the *Compositae* family which have turned out to contain acetylenic compounds, the genus *Coreopsis* is leading as to the number of isolated polyacetylenes¹⁻⁴. The genus *Coreopsis* belongs to the tribus *Heliantheae*, subtribus *Coreopsidinae*. In this subtribus the botanists have since long ago placed the genera *Coreopsis*, *Bidens* and *Cosmos* close together. As a matter of fact the opinion of the botanical experts has varied very much as to where in the three genera a given species has to be placed, and the examples are numerous where a species has synonymous names in all three genera⁵. So it was tempting to investigate some members of the genus *Bidens* to see if they did contain polyacetylenes, and if so, whether they were of the types earlier found in *Coreopsis*.

The UV spectra of the crude essential oils or acetone extracts of *Bidens ferulaefolia* Thuill and *B. radiata* (Jacq.) DC. at once revealed the presence of compounds with polyacetylenic chromophores. By chromatography some of these could be isolated in a pure state.

The trideca-1,11-diene-3,5,7,9-tetrayne (I, R = H) which was first isolated from some annual *Coreopsis* species ¹



was found in the root and the flowers as well as in the green parts of both the *Bidens* species investigated.

In the root extract of *B. radiata* and *B. ferulaefolia* and in the essential oil of the green parts of the latter there was found a polar compound with exactly the same UV spectrum as I. A similar compound has recently been isolated by J. Stene Sørensen from some perennial *Coreopsis* species, and is supposed to be I, R = OCOCH₃. In no case so far the amount of this polar form of I has been sufficient for isolation of the substance in pure, crystalline form.

From the essential oil of the flowers and green parts of *B. ferulaefolia* a crystalline compound of m.p. 70°C could be isolated which through its UV spectrum and the spectrum of its maleic anhydride adduct could be identified with the diyne-tetraene II first isolated ¹ from the green part of some annual *Coreopsis* varieties.

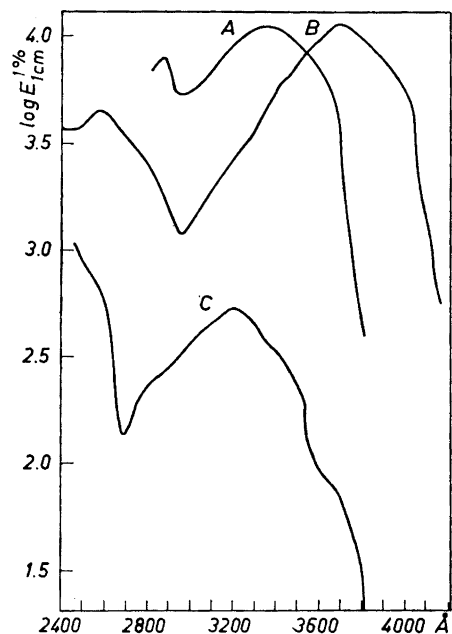


Fig. 1. Ultraviolet absorption in hexane of:

- A. Compound with λ_{max} at 3 350 Å.
- B. Compound with m.p. 42°C.
- C. Compound with m.p. 42°C after hydrogenation.

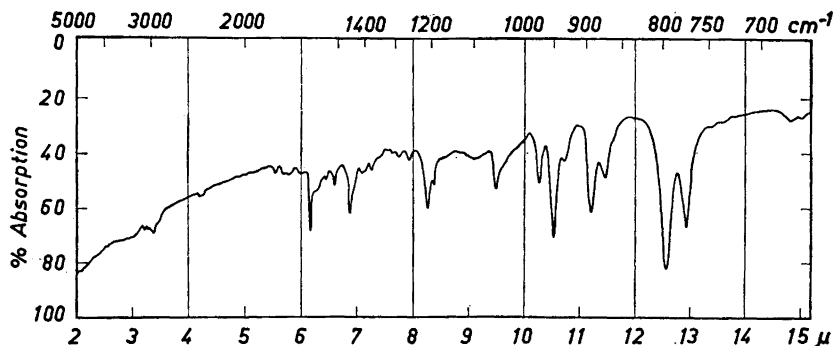


Fig. 2. Infrared absorption in KBr of compound with m.p. 42°C.

The green parts of *B. ferulaefolia* gave some fractions with UV spectra which seemed to indicate mixtures of II with phenyl-heptatriyne III characteristic of some perennial *Coreopsis* species³. The amount of these fractions was too small to allow the isolation of III in pure form. J. Stene Sørensen has, however, isolated III in a pure form from members of the genus *Bidens*⁶, viz. *B. cernua* L. and *B. pilosa* L., thus III is also a polyacetylenic compound common to the genera *Coreopsis* and *Bidens*.

When the extracts from leaves and flowers of *B. radiata* were chromatographed on deactivated alumina, fractions were obtained on elution with 10–50 % benzene in petroleum ether which had only one very broad maximum in UV. From the 10 %-benzene eluates there could be isolated very small amounts of a substance with one broad maximum in UV in hexane solution at 3 350 Å, cf. Fig. 1. The amount of substance was too small for further investigations.

The eluates with 25 and 50 % benzene on evaporation afforded slightly yellow crystals, m.p. 42°C (evacuated tube). When tested in an open melting point tube, the substance only darkened without melting below 350°C.

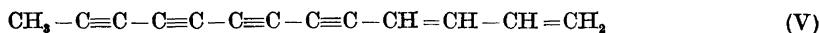
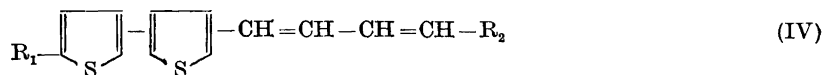
The UV spectrum in hexane is reproduced in Fig. 1 and shows no relationship to the fine-structure spectra of polyacetylenic compounds. The IR spectrum had no absorption in the triple bond region, but maxima at 3 120, 1 513, 1 210 and 771 cm^{-1} were indicative of 2,5-disubstituted thiophene. Other bands characteristic of double bonds were present, but carbonyl or other characteristic groups were absent.

That the substance was really a sulphur containing compound, was confirmed by a quantitative sulphur determination (J.S.S.) giving 26.4 % S. This sulphur content is so high that the molecule must contain 2 sulphur atoms, since the molecular weight of about 120 calculated for one sulphur atom is too low to build up a chromophore with first maximum at 3 690 Å.

By catalytic hydrogenation with Pd/BaSO₄ the UV maximum moved down to 3 190 Å. A similar displacement was found in the reaction with maleic anhydride; first maximum of the crude adduct at 3 150 Å. The new substance thus seems to contain a butadienyl-grouping linked with a chromophore resistant to mild hydrogenation.

According to Sease and Zechmeister ⁷ dithienyl has one broad UV maximum at 3 010 Å. One alkyl group displaces this maximum 40–50 Å towards longer wavelengths; thus a 5,5'-dialkyl-2,2'-dithienyl should absorb around 3 100 Å.

The meagre experimental evidence thus point to a general formula IV.



Bands of medium strength at 890 and 976 cm^{-1} in the IR spectrum of IV may indicate a vinyl group, that is $\text{R}_2 = \text{H}$. The sulphur content gives a molecular weight for 2 S intermediate between $\text{R}_1 = \text{CH}_3$ (232.35) and $\text{R}_1 = \text{C}_2\text{H}_5$ (246.47). Since all the polyacetylenic compounds from *Coreopsis* have C_{13} skeletons, and 4 of these, as mentioned above, occur in *B. radiata* and *B. ferulaefolia* we are inclined to assume that $\text{R}_1 = \text{CH}_3$, and that the compound, m.p. 42°C, is 5-methyl-5'-buta-1,3-dienyl-2,2'-dithienyl=IV, $\text{R}_2 = \text{H}$, $\text{R}_1 = \text{CH}_3$.

As the content of IV in the essential oil of *B. radiata* is rather small, and it thus would take a long time to collect enough of the natural substance for further constitutional work, IV was synthesized by Lars Skatteböl, and, as shown in a later communication ⁸, synthetic IV agrees in most properties well with those observed for the *B. radiata* substance. A minor difference in the IR spectra might be due to the fact that the natural substance because of the small amount available had to be measured as solid in a potassium bromide disk, whereas the synthetic substance was measured in carbon disulphide solution.

IV is the first derivative of dithienyl to be found in nature*. Since the thiophene derivatives found in the *Compositae* seem to be closely related to aliphatic poly-ene-ynic compounds ⁴, attention might be drawn to the formal relationship between IV, $\text{R}_1 = \text{CH}_3$, $\text{R}_2 = \text{H}$ and trideca-1,3-diene-5,7,9,11-tetrayne V. V has not so far been identified with a naturally occurring compound. In previous investigations ^{9,2} we have demonstrated that isomeric

compounds $\text{R}-\text{C}\equiv\text{C}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ and $\text{R}-\text{C}_6\text{H}_5$ occur in *Compositae*

plants indicating their possible origin from a common precursor. The phenyl isomer corresponding to V is the 1-phenylhepta-1,3,5-triynyl III which so far is known only from *Bidens* and *Coreopsis* species.

EXPERIMENTAL

General method. The essential oils of the flowers and the green parts were isolated by steam distillation, whereas the roots were given 3 successive extractions with acetone on standing at room temperature for one day. The bulk of the acetone was removed in a vacuum, and the remaining solution shaken with petroleum ether after dilution with much water. The combined petroleum ether extracts were washed with water and dried over anhydrous sodium sulphate. Petroleum ether solutions were chromatographed on

* Since this work was carried out in 1955, another derivative of dithienyl has been isolated from *Tagetes* (African Marigolds) by J. H. Uhlenbroek and J. D. Bijloo [*Rec. trav. chim.* **78** (1959) 382].

alumina, slightly deactivated according to the method of Mancera *et al.*¹⁰; retention volume of the packed column 200 ml. Elution was carried out with mixtures of petroleum ether containing benzene in stepwise increasing amounts. At every concentration level 450 ml eluant were added, and the eluate was cut into three fractions of 150 ml each.

Bidens radiata Thuill.

Seed sample (*Hort. Bot. Univ. Osloensis*) cultivated on open ground at N.T.H. during the summer 1955.

Flowers. 1.2 kg of fresh flowers afforded 1.32 % of essential oil. A solution in petroleum ether was chromatographed on deactivated alumina. The first fraction with 10 % benzene in petroleum ether gave 2.2 mg of residue with a UV spectrum of pure I; calculated content in the fraction 0.82 mg. The residue crystallised, but the small amount of crystals which rapidly became dark in light, could not be investigated further.

The following fractions with 10 % benzene showed only two broad and undistinct absorption bands in UV. The total amount of substance in these fractions was only some 10 mg. But from these residues a small amount of white crystals could be isolated which in UV showed two broad maxima at 3 395 and 2 900 Å and some slight inflexions presumably caused by chromophore I. The amount was insufficient for further work.

The first fraction with 50 % benzene showed only one broad absorption band in UV at 3 650 Å. From the small residue (23.2 mg) a slightly yellow crystalline compound, m.p. 42°C, could be isolated by crystallisation from petroleum ether. According to the m.p. and the UV spectrum it is identical with one of the substances from the leaves, *vide infra*.

Leaves and stems. 2.3 kg of the green parts furnished 0.05 % of essential oil. Chromatography on alumina was carried out as above. The eluate with petroleum ether showed on absorption above 2 200 Å. The first fractions with 10 % benzene in petroleum ether gave UV spectra conform with that of I. From the absorption spectra a total content of 2.8 mg I was calculated, that is 0.24 % of the essential oil.

The final fraction with 10 % benzene in petroleum ether contained the same broad-banded chromophore as found in the flowers, first maximum at 3 350 Å; Fig. 1, curve A. The amount of material was small (5.3 mg), and the substance could not be obtained in the crystalline state.

The eluates with 25 % and with 50 % benzene in petroleum ether contained the other broad-banded chromophore found in the flowers. The total amount of material was about 55 mg. When this oily residue was dissolved in low boiling petroleum ether (40–60°C) and the solution stored at –10°C, 7.5 mg of slightly yellow crystals resulted. Attempts to do a m.p. determination in the usual open tube was unsuccessful; the crystals only darkened and turned slowly into carbonaceous material without melting. In an evacuated tube a rather sharp m.p. of 42°C was observed. UV spectrum, Fig. 1, curve B, $\lambda_{\max} = 3\ 690\ \text{Å}$, $\log E_{1\ \text{cm}}^{1\ \%} = 4.04$, $\lambda_{\max} = 2\ 580$, $\log E_{1\ \text{cm}}^{1\ \%} = 3.63$; IR spectrum Fig. 2.

Maleic anhydride adduct: 1 mg of crystals was dissolved in 0.5 ml of pure benzene with 55 mg of freshly sublimed maleic anhydride in a tube and sealed under pure nitrogen. It was left in a water bath at 70°C for 4 h. The reaction solution was measured directly in the spectrometer; the maximum at 3 690 Å had disappeared. The solvent and the excess of maleic anhydride was removed in a vacuum at room temperature. The minute residue dissolved in alcohol showed λ_{\max} at 3 150, inflexion at 3 050 Å.

Catalytic hydrogenation: 4.9 mg of crystals were hydrogenated in alcoholic solution with a Pd-catalyst. A quantitative determination of the consumption of hydrogen could not be carried out. The hydrogenation product was a viscous oil, UV spectrum, see Fig. 1, curve C.

Roots. 0.57 kg of fresh roots were extracted with acetone, and the extract transferred to petroleum ether, yield of crude extract 0.14 %.

Chromatography on alumina was carried out as above. The eluate with petroleum ether had no selective absorption in UV. The first fraction with 10 % benzene gave 25.4 mg of oily residue with the characteristic spectrum of I, calculated content 0.56 mg, that is 0.07 % of the root extract. Small amounts of the characteristic, unstable crystals of I could be isolated from petroleum ether in a refrigerator.

The further fractions with 10 % to 50 % benzene in petroleum ether appeared to contain a complicated mixture of compounds with different chromophoric systems. The material was insufficient for isolation of any of these in a pure state. When more starting material becomes available, a reinvestigation will be attempted.

Undiluted benzene eluted some 180 mg of an oil with a very indistinct spectrum of I. The calculated amount of this chromophore using the extinction coefficient of I, $R = H$, was only about 1.5 mg. As, however, it was of interest to ascertain that a polar compound with the diene-tetraene-chromophore was present, a rechromatography was carried out, taking three fractions with 70 % benzene in petroleum ether and then three with undiluted benzene. The whole of the compound with the diene-tetraene-chromophore was obtained in the third of the 70 % benzene fractions. The total amount of substance in this eluate was only a few mg. The UV spectrum was completely conform to I, $R = H$, and the calculated concentration in this fraction was 31 %. The residue was a viscous oil. The amount of substance was too small for further experiments.

Bidens ferulaefolia (Jacq.) DC.

Seed sample (*Hort. Bot. Univ. Osloensis*) cultivated on open ground at N.T.H. during the summer 1955.

Flowers. 530 g of fresh flowers gave a 0.053 % yield of essential oil, which was chromatographed on alumina as above. The eluate with petroleum ether showed no selective absorption in the UV region. The first fraction with 10 % benzene showed the characteristic spectrum of I, $R = H$, calculated content 0.8 mg, that is 0.3 % of the essential oil.

The subsequent fractions with 10 % benzene in petroleum ether and the first fraction with 25 % benzene had rather indistinct spectra in UV, but some of the main maxima agreed with those of the diene-tetraene II. By crystallisation from petroleum ether in a refrigerator some 4 mg of slightly yellow crystals were obtained which showed a somewhat unsharp m.p. of 68–69°C; pure II has m.p. 71–72°C. The UV spectrum of this crystalline compound agreed very well with that of II.

Maleic anhydride adduct: 2.5 mg of the crystals were dissolved in 0.5 ml of pure benzene and 53 mg of maleic anhydride were added. The solution was prepared in a tube which was sealed under pure nitrogen. The tube was left for 5 h at 72°C and worked up as above. The residue was washed with cold petroleum ether which removed unreacted II. The insoluble residue showed the characteristic maxima of an ene-diyne-ene-grouping.

Leaves. 2.7 kg of green parts (leaves and stems) gave 0.14 % of essential oil separated by chromatography as above. As with the flowers the eluate with petroleum ether showed no selective absorption in the UV region.

The first fraction with 10 % benzene in petroleum ether showed the characteristic spectrum of I, $R = H$. The calculated amount of I was only 0.3 mg and was insufficient for further investigation.

The following fractions with 10 % benzene in petroleum ether had UV spectra in which very sharp peaks in the positions characteristic of III were superimposed on the indistinct spectrum of the diene-tetraene II. Although crude crystals of II could be obtained, they always contained small amounts of III which gave extra peaks in the UV spectra.

Rechromatography using 8, 10 and 20 % benzene in petroleum ether as eluants gave a fairly complete separation. The first eluates showed UV spectra conform to that of phenylheptatriyne III whereas the final ones were conform to that of II.

The eluate with 50 % benzene had no selective absorption. With undiluted benzene there appeared small amounts of a substance with the distinct spectrum of the diene-tetraene I. Thus also in this case a derivative of I with a polar substituent ($R = OCOCH_3$?) is present.

Roots. 530 g of fresh roots were extracted with acetone, and the lipoids transferred to petroleum ether; crude extract 0.34 %. Chromatography carried out as above gave an unusually simple picture. The characteristic spectrum of the diene-tetraene I appeared in the first fraction with 10 % benzene, and the final fraction with 10 % benzene and all fractions with 25 % and with 50 % benzene showed no selective absorption. Undiluted benzene then eluted a compound with UV spectrum identical with that of I. The roots thus seem to contain only two polyacetylenic compounds, a non-polar and a polar type of I. The amount of polar I was too small for further study.

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