

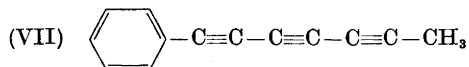
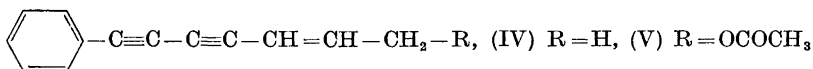
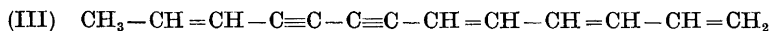
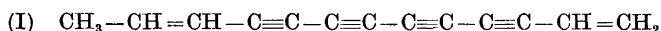
Studies Related to Naturally Occurring Acetylene Compounds XXIII. 1-Phenylhepta-1:3:5-triyne from *Coreopsis grandiflora*, Hogg ex Sweet

JÖRGINE STENE SÖRENSEN and NILS ANDREAS SÖRENSEN

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

A preliminary investigation of some perennial species belonging to the genus *Coreopsis* revealed the occurrence of 1-phenylhepta-1:3:5-triyne (VII) in Nature. The constitution of this new polyacetylene has been confirmed by synthesis.

In the XVIIth communication of this series Sørensen and Sørensen¹ described the isolation of 4 new polyacetylenic compounds from some annual garden varieties of the genus *Coreopsis* L., family *Compositae*. As shown in the preceding communication² one of these compounds turned out to be a mixture of two previously unknown polyacetylenes raising the number of acetylenic compounds with established structure in annual *Coreopsis* species to the 5 compounds (I)–(V).



In that preliminary work only one single perennial *Coreopsis* species was investigated, viz. *C. verticillata* L. The tetrayne (I) was present in the roots, but otherwise *C. verticillata* differed remarkably from the other *Coreopsis* species through a high content of 2:6-dimethyloctatetraene = Cosmene, first isolated

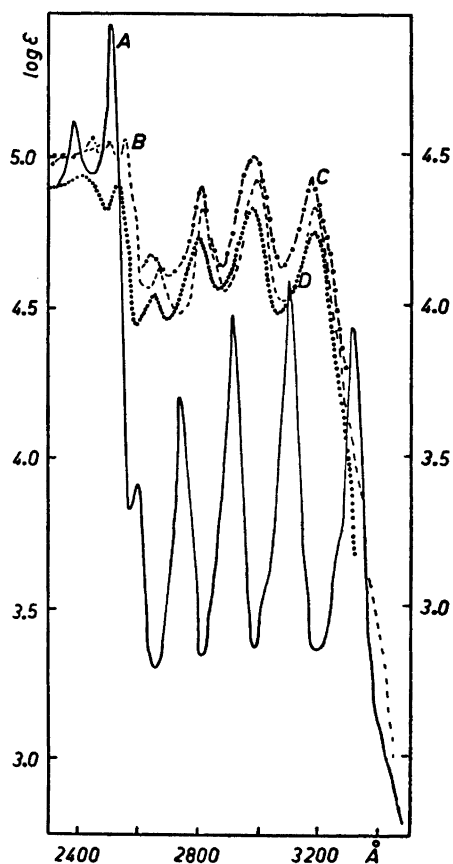


Fig. 1. Ultraviolet absorption in hexane of

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|--------------------------------------------------------------|-------------------|
| A. 1-Phenyl-hepta-triyne-1:3:5 (VII) ————— | (scale left side) |
| B. 6(?)-chloro-1-phenyl-hepta-1:3-diyn-5-ene - - - - - | » » » |
| C. 1-Phenyl-hepta-1:3-diyn-5-en-ol-7-acetate (V) - . - . - . | » » » |
| D. 1-Phenyl-hepta-1:3-diyn-5-ene (IV) | » » » |

from *Cosmos bipinnatus*, but so far only found in traces in one annual *Coreopsis*, viz. *C. Drummondii*³.

The next perennial *Coreopsis* which incidentally was investigated was *C. grandiflora*, Hogg ex Sweet. Although the tetrayne (I) was readily recognisable in the long-wave part of the spectrum of the primary acetone extracts from the root part, the U.V.-spectra of all parts of *C. grandiflora* were dominated by a fine structure spectrum, cf. Fig. 1, curve A, so far not found in the investigated annual members of the genus. By chromatography on alumina the new chromophore followed immediately after small fractions containing the characteristic absorption bands of the tetra-acetylene (I) and the penta-acetylene (VI). The occurrence of (VI) seems to be characteristic of tribus *Inuleae* but

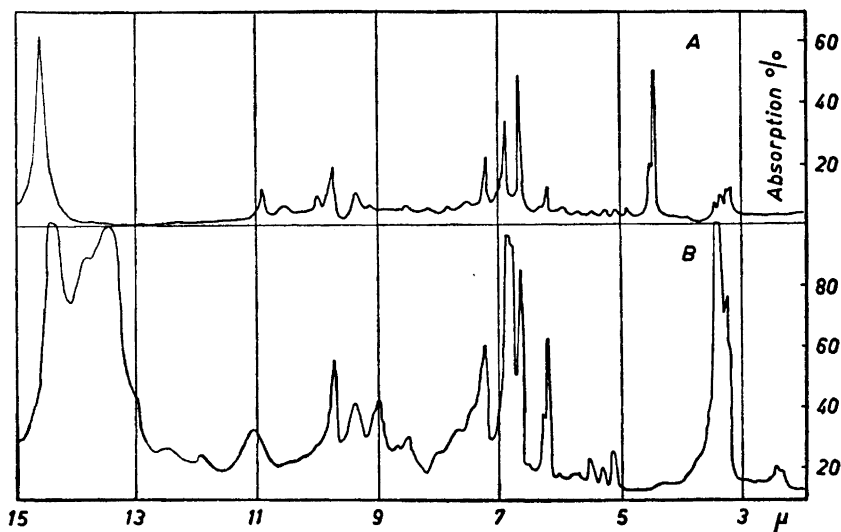


Fig. 2. Infra red absorption of

- A. 1-Phenyl-hepta-1:3:5-triyn in CHCl_3 , $c = 11\%$, $l = 0.05$ mm
 B. 1-Phenyl-*n*-heptane, liq. $l = 0.025$ mm.

has not so far been found in the genus *Coreopsis* itself; it has already been found in other members of tribus *Heliantheae* including representatives of sub-tribus *Coreopsidinae*. A number of chromatographic fractions eluted with 10% benzene in petroleum ether immediately delivered the new chromophore in crystalline condition. Recrystallisation from petroleum ether gave colourless prisms m.p. 55–56°C.

The ultraviolet spectrum was much sharper in fine structure than that of the 1-phenylocta-1:3:5-triyn synthesised by Bruun, Skatteböl and Sørensen⁴ but identical in position of the maxima within the limits of the experimental errors:

$\text{C}_6\text{H}_5-(\text{C}\equiv\text{C})_3-\text{CH}_2-\text{CH}_3$	λ_{max} :	3 315	3 100	2 905	2 735	2 595	2 510	2 387	Å
<i>C. grandiflora</i> , m. p. 55–56°	λ_{max} :	3 309	3 097	2 908	2 735	2 590	2 504	2 380	Å

That the new compound did contain the phenyl group was obvious from strong peaks in the infrared at 1 495 and 686 cm^{-1} , cf. Fig. 2, curve A.

Catalytical hydrogenation gave a liquid hexahydrocompound with a consumption of 5.9 mole hydrogen (calc. as C_{13}H_8). The infrared spectrum of this hexahydrocompound agreed almost completely with that of 1-phenyl-*n*-octane. These few facts strongly indicated the structure 1-phenylhepta-1:3:5-triyn (VII). This compound was synthesised along the same route which was used for the homologue⁴, viz. reaction of phenylpropargylaldehyde with the di-Grignard derivative of but-1-yn-3-ol to give 1-phenylhepta-1:4-diyne-3:6-diol. Through the dichloride this glycol was converted into 1-phenylheptatriyne.

The intermediate glycol could not be obtained crystalline and although the synthesis was successful and the synthetic 1-phenylheptatriyne was identical with the new hydrocarbon from *C. grandiflora* a number of side reactions were met with. Some of these are described in the experimental part.

1-Phenylheptatriyne is a rather stable compound. It is volatile with steam and so it may also be isolated from essential oils. Due to the characteristic U.V.-spectrum it is easily recognised also when present in small quantities. For this reason we do not think it is a general component of the essential oil of all members of the genus *Coreopsis*. Rather it seems more abundant in the perennial members than in the annual. Of *C. tripteris* L. only a few plants were available and (VI) was present only in traces.

In *C. lanceolata* L. and *C. saxicola* Alex., of which the first is botanically closely related to *C. grandiflora*, the oils were in part so enriched in (VII) that it crystallised out when stored in a refrigerator.

That (VII) is not restricted to some section of the genus *Coreopsis* was established by a preliminary investigation of some members of the genus *Bidens*, some of which turned out to be very rich in VII. These investigations will be described in later communications of this series.

The botanists long ago have placed the 3 genera: *Bidens*, *Coreopsis* and *Cosmos* close together and many of their species have synonymous names in all three genera. A close relation *Bidens*-*Coreopsis* has been confirmed by the investigations of their acetylenes; so far, however, the few members of *Cosmos* which have been investigated have not shown any of those extensive variations in polyacetylenes which make *Bidens* and *Coreopsis* a promising field of further studies.

EXPERIMENTAL

Coreopsis grandiflora, Hogg ex Sweet, flowers. The flowering heads collected medio June 1954 were extracted with acetone and the lipids transferred to petroleum ether. The crude extract (0.75 % of the fresh flowers), which was still deep orange from flower pigments, was chromatographed on alumina from petroleum ether solution. Washing with petroleum ether removed rather large amounts of colourless hydrocarbons (28 %). No chromophore appeared until the content of benzene in the eluting mixture was raised to about 10 %. In the first fraction the U.V.-maxima of the tetra-yne (I) which were just traceable in the spectrum of the crude oil, came out very clearly, however, with faint extra maxima belonging to the penta-yne (VI). This penta-yne, with the characteristic first maximum at 4 100 has been found in a lot of tribes of the *Compositae*, but so far not in the genus *Coreopsis*. As the calculated amounts of (I) and (VI) were far below 1 mg no attempt was made to isolate them in the crystalline state.

The subsequent washings with 10 % benzene in petroleum ether contained the new hydrocarbon, which on evaporation crystallised immediately. Recrystallisation of the residues from petroleum ether gave long, colourless prisms, m. p. 55°–56°, unchanged on further recrystallisation.

U.V.-Spectrum, Fig. 1, curve A, infrared Fig. 2, curve A. Catalytical hydrogenation: 222.9 mg were hydrogenated with Pd/BaSO₄ catalyst; consumed 232 ml calculated for C₁₃H₈, 6 l¹ = 237 ml (759 mm, 21.5°C). The hexahydro compound was isolated in the usual way and the oil distilled. U.V.-Spectrum typical toluene type, λ_{max} 2 683 Å, log ε_{max} = 2.315. Infrared, Fig. 2, curve B.

Another batch of flowers of *C. grandiflora* was distilled in steam, yield 0.75 % of the essential oil (1.5 g) was stored in a refrigerator at -18°; phenyl-tri-yne (VII) after some time crystallised directly from the crude oil. Further amounts could be obtained in pure condition by chromatography as above. Total amount 0.22 g or close to 15 % of the essential oil.

Synthesis of 1-phenylhepta-1:3:5-triyn-3-ol. But-1-yn-3-ol was prepared according to Campbell *et al.*⁵ Phenylpropargyl aldehyde was prepared from α -bromo-cinnamic aldehyde (*Org. Syntheses* 25, 92) via the ethylene glycol acetal⁶. The dehydrobromination of this acetal was effected by boiling 113 g of the acetal with a solution of 50 g of potassium hydroxide in 500 ml of ethanol for 75 min. The phenylpropargyl aldehyde ethylene acetal was extracted with chloroform, dried and distilled, yield 96 %. The hydrolysis was carried out as for the diethyl acetal.

1-Phenylhepta-1:4-diyne-3:6-diol. 23 g of ethyl bromide was grignardised with Mg in 40 ml of dry ether. 7 g of but-1-yn-3-ol was added slowly during 1 h with external cooling. Dry tetrahydrofurane, 3 \times 50 ml, was added to keep the Grignard compound in solution. To this solution 13 g of phenyl-propargyl aldehyde were added slowly, the temperature not being allowed to raise above 5°C. The reaction mixture was left for 12 h at room temperature, then decomposed with ammonium chloride and extracted with ether. The product was a viscous oil which could not be brought to crystallisation. In preliminary experiments purification by chromatography and high vacuum distillation was attempted, but with no success.

The crude diol was dissolved in 200 ml of dry ether, 10 ml of dry pyridine was added, and the temperature was brought down to -35°. As addition of thionyl chloride still gave vigorous reaction and dark tars, the thionyl chloride was diluted with 5 parts of dry ether and the reaction continued at -50 to -70°. The solvent was evaporated at 0° by suction. The oily residue was slowly added to a solution of 8 g of potassium in 140 ml of absolute alcohol at -30° and the reaction mixture stirred for half an hour during which the temperature rose to -20°. Pure nitrogen was led through the solution which was allowed slowly to reach 12° (1.5 h). It was decomposed with water and extracted with ether in the usual way.

The U.V.-spectrum of the crude reaction product was disappointingly unsharp, the unusual sharp peaks of the *C. grandiflora* substance being just noticeable. Chromatography on alumina removed all discolouring impurities but the fraction eluted with 10 % benzene in petroleum ether still had a very complex spectrum. Rechromatography and redistillation at first furnished 2 crystalline substances. The final chromatographic washings with 10 % benzene afforded fractions with U.V.-spectra identical with the *C. grandiflora* substance. These fractions gave a crude crystallisate, m. range 38-45°, after one recrystallisation from petroleum ether m. p. 52-53°, recrystallisation m. p. 55-55.5°, mixed m. p. 1:1 mixture 55 to 55.8° sharp. Infrared and U.V.-spectra identical within the errors of observation.

Whereas the main chromatographic fractions still gave very complex spectra, the first fractions with 10 % benzene gave oils devoid of the phenyl-triyn-3-ol chromophore. These could be induced to crystallise from petroleum ether in the low temperature refrigerator. The crystals did not show a sharp m. p., range 45-49°, but could be recrystallised to a rather sharp m. p. 61-62°. (Found: C 79.8; H 5.05. Infrared gave no indication of hydroxylic or carbonyl oxygen. The Beilstein test revealed halogen. Calc. for $C_{13}H_8Cl$: C 77.8; H 4.52.) As evident from the U.V.-spectrum, *cf.* Fig. 1, curve B, the substance must contain a phenyldiyn-ene chromophore, $C_6H_5-C\equiv C-C\equiv C-C=C-R$. In Fig. 1, curve C, *trans* 1-phenylhept-5-ene-1:3-diyn-7-ol acetate¹ and *trans* 1-phenylhept-5-ene-1:3-diyne² are given for comparison, both previously isolated from annual *Coreopsis* species and the constitution proved by total synthesis. It thus seems very probable that the crystalline side product, m. p. 61°, is 6-chloro-1-phenylhept-5-ene-1:3-diyne.

The liquid fractions were measured in the infrared. A band at 1960 cm^{-1} indicated the presence of allenes; the nearest possibility should be 1-phenylhepta-5:6-diene-1:3-diyne. However, this liquid fraction did not give further amounts of 1-phenyl-hepta-triyn-3-ol by treatment with potassium hydroxide.

Coreopsis grandiflora; leaves. The leaves and stems were distilled in steam; the essential oil amounted to 1.2 ‰. The U.V.-spectrum of the essential oil was nearly conformed with that of phenylheptatriyne (VII), calculated content 6.3 %. Chromatography as above furnished 440 mg of pure (VII).

Coreopsis grandiflora, root. The roots were extracted with acetone and the lipids transferred to petroleum ether. Yield 1.3 %. The U.V.-spectrum of the crude extract was dominated by the characteristic bands of (VII), but those of both (I) and (VI) could be recognised. Chromatography as above afforded 215 mg = 2.5 % of pure (VII). The components of some of the minor fractions will be treated in a following communication.

Coreopsis saxicola, leaves. The plants were cultivated at N.T.H., Trondheim, on open ground and harvested on September 16th 1955. Only very few flowers had appeared, altogether weighing 16 g from which 12 mg of essential oil was prepared. The U.V.-absorption of this small amount of essential oil from the flowers came very close to that of the leaves and so no further investigation of the flower oil was carried out.

5.2 kg of fresh leaves gave 0.7 ‰ of essential oil. The crude essential oil gave a sharp U.V.-absorption spectrum dominated by phenylhepta-tri-ene, calc. concentration of (VII) = 25 %. Incidentally this oil was stored for a long time in a refrigerator (-15°C) and then had deposited a layer of crystals, which after one recrystallisation from petroleum ether, melted at 54°. Mixed m. p. with authentic phenyl-heptatriene (VII) 53–54°; ultraviolet and infrared spectra identical.

The mother liquor was chromatographed on deactivated alumina. The eluates with 8–10 % benzene in petroleum ether gave U.V.-spectra of pure (VII), all crystallised, giving altogether 1 g of pure (VII).

Coreopsis lanceolata, leaves. The plants were cultivated at N.T.H., Trondheim, on open ground and harvested during September 1955. Yield of essential oil 0.25 ‰. The oil was chromatographed on deactivated alumina and eluted with mixtures of petroleum ether and benzene. The eluates with less than 8 % benzene were devoid of absorption in the ultraviolet. All fractions eluted with petroleum ether with 8 % benzene gave the U.V.-spectrum of pure (VII) and all of them crystallised directly on evaporation, giving altogether some 100 mg of pure (VII) m. p. 55°, undepressed by authentic phenylhepta-tri-ene.

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