

Studies Related to Naturally Occurring Acetylene Compounds. XVII. Four New Polyacetylenes from Garden Varieties of *Coreopsis*

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Some common garden *Coreopsis* species have furnished mixtures of new polyacetylenic compounds. Four of these have been obtained in a pure state. Dodeca-1:11-diene-3:5:7:9-tetraene (II) dominates in the roots of all the investigated *Coreopsis* species; through the characteristic U.V.-spectrum (II) was also detected in small amounts in the thistles: *Carthamus lanatus* L., *Cnicus benedictus* L. and *Silybium Marianum* Gaertn. 1-Phenyl-*n*-hept-5-ene-1:3-diyn-7-ylacetate (V) could be isolated from all parts of the said *Coreopsis* species. The constitution and *trans* configuration of (V) was established through comparison with synthetic (V). Trideca-1:3:5:11-tetraene-7:9-diene (IX) dominates in the oil from the leaves, whereas 1-phenyl-*n*-undeca-7:9-diene-1:3:5-triyn (XI) was the main chromophore of the oil from the flowers.

In the preceding communications of this series the occurrence of different types of acetylenic compounds in some plants belonging to the *Compositae* has been demonstrated. With the object of gathering information about the distribution of these compounds within the different tribes and subtribes of this vast family some common garden plants from different tribes lacking wild representatives in this country have been investigated. As different species of the genus *Coreopsis* have been investigated previously¹ with regard to their peculiar flower pigments, the so-called antochlor pigments, we were somewhat surprised when it turned out that this genus is rich in new members of the naturally occurring polyacetylenes.

The species investigated were the annuals *Coreopsis tinctoria* Nutt. in the garden varieties "nigra speciosa" "nana radiata" and *Coreopsis Drummondii* Torr & Gray, *C. cardaminifolia** *atrosanguinea* and a small sample of the perennial *C. verticillata* L.

Since all these garden varieties are glabrous plants we were surprised to obtain good yields of essential oils, ~ 0.6⁰/₁₀₀. The essential oils from all parts of the plants showed selective absorption in ultraviolet partly with acetylenic

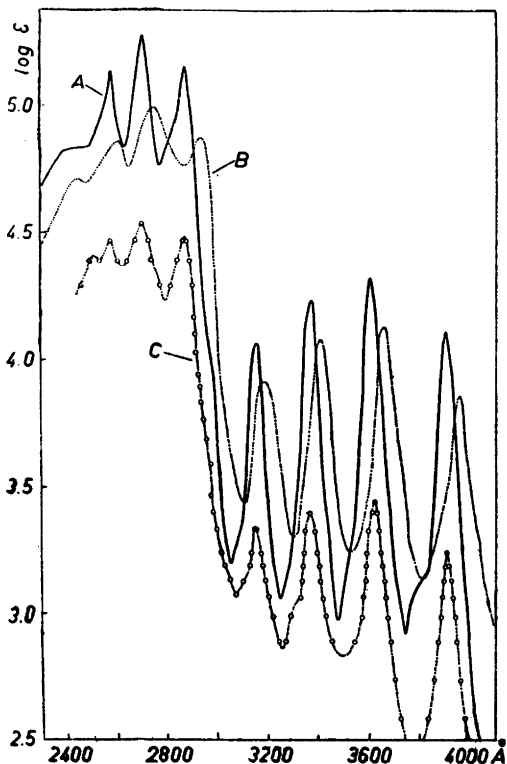
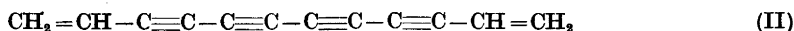


Fig. 1. Ultraviolet absorption of

- A: dodeca-1:11-diene-3-5-7:9-tetrayne (II) from *Coreopsis* in hexane.
 B: tetradeca-2:12-diene-4:6:8:10-tetrayne (I) in alcohol, E. R. H. Jones *et al.*
 C: purest fraction of (II) from *Cnicus benedictus* L.

spacing between the maxima. Since the spectral curves of the oils from different parts of the plants differed rather much, the oil from the roots and flowers and the green part of the plants were worked up separately. This separation greatly facilitated the isolation of some of the new polyacetylenes, but, as will be seen from the chromatographic separation described in the experimental part, the four compounds so far isolated occur in all parts of the plants but varying in dominance.

The crude oil from the roots exhibited sharp absorption maxima in U.V.; the substance responsible for these maxima is only slightly retarded by chromatography on alumina from petroleum ether solution. The U.V. spectrum of the pure substance in hexane is given in Fig. 1, curve A, together with the spectrum of tetradeca-2:12-diene-4:6:8:10-tetrayne (I) synthesised by E. R. Jones *et al.*².



We are greatly indebted to professor E. R. H. Jones who has put the full curve for (I) at our disposal. The conformity of the two curves is striking. The displacement of the maxima of I, 40—50 ÅU towards longer wave-lengths, are in all probability mostly due to the use of different solvents (alcohol with I, hexane with II).

This sharp-banded substance from *Coreopsis* roots has, when pure, an excellent crystallising power. The crystals, which are slightly yellow, are, however, very unstable. They become dark rapidly between 43 and 45°, and turn brownish-black between 45 and 48° without any further change.

By catalytical hydrogenation 10.1 moles H₂ were consumed. The perhydro-compound melted at —10.8 to —10.3°, synthetic dodecane at —10 to —9.3°, mixed m.p. —12.3 to —11.5°. Dr. W. D. Celmer, Chas. Pfizer & Cie, New York, most kindly measured the infra-red spectra of the perhydrocompound and of our synthetic dodecane which confirmed the identity.

From the conformity of the U.V.-spectra, cf. Fig. 1, we conclude that the *Coreopsis* hydrocarbon also must be a diene-tetrayne. Of the possible arrangements of the double and triple bonds that of II = dodeca-1 : 11-diene-3:5:7:9-tetrayne has been chosen for the following reasons. Schlubach *et al.*³ demonstrated that the triple bond reacts much more slowly than the double bond with peracetic acid. The *Coreopsis* substance reacted very slowly with peracetic acid. The small amounts of substance available did not permit the isolation of a crystalline dioxide; but as soon as the 3 915 ÅU maximum had disappeared, the remaining chromophoric system exhibited maxima at 2 450, 2 330 and 2 235 ÅU, close to the position of the strong short-wave band group of dialkyl tetraacetylenes (2 410, 2 300 and 2 200 ÅU)⁴.

Therefore we conclude that the four triple bonds are conjugated. It then remains only two constitutional possibilities, II and dodeca-1 : 3-diene-5 : 7 : 9 : 11-tetrayne. The experiences accumulated from the synthetic side during recent years^{2, 3, 5} strongly suggest that a mono-alkyl tetrayne would be much too unstable to exist above 0° C.

There occurs in the infra-red spectrum of this diene-tetrayne, cf. Fig. 2, curve A, a definite peak at 2 130 cm⁻¹ close to the position characteristic of mono-alkylated acetylenes, but infra-red data on synthetic and naturally occurring polyacetylenes of the di-alkylated type^{7, 8} very often have peaks near 2 100 besides the 2 200 cm⁻¹ peak. Through the courtesy of the Jackson Laboratory of the E. I. du Pont de Nemours & Co. Inc. we obtained an infra-red spectrogram of divinyl-acetylene, redrawn in Fig. 2 curve B. The agreement in the region 7—15 μ is good and indicates that the *Coreopsis* hydrocarbon has both double bonds as vinyl groups.

Thus, although the small amounts available and the extreme instability of this *Coreopsis* hydrocarbon in the crystalline state have seriously hampered our investigations, we think that (II) is fairly established as its constitutional formula*.

The extremely sharp U. V. absorption maxima of (II) facilitates the spectroscopic detection of this hydrocarbon. So far this spectrum has been found in

* Note added in proof: II has in the meantime been synthesised by Jones, Thomson and Whiting, *vide* this volume p. 1944. From the data of synthetic II Jones *et al.* concluded that the *Coreopsis* hydrocarbon might be a mono-alkyl-diene-tetrayne.

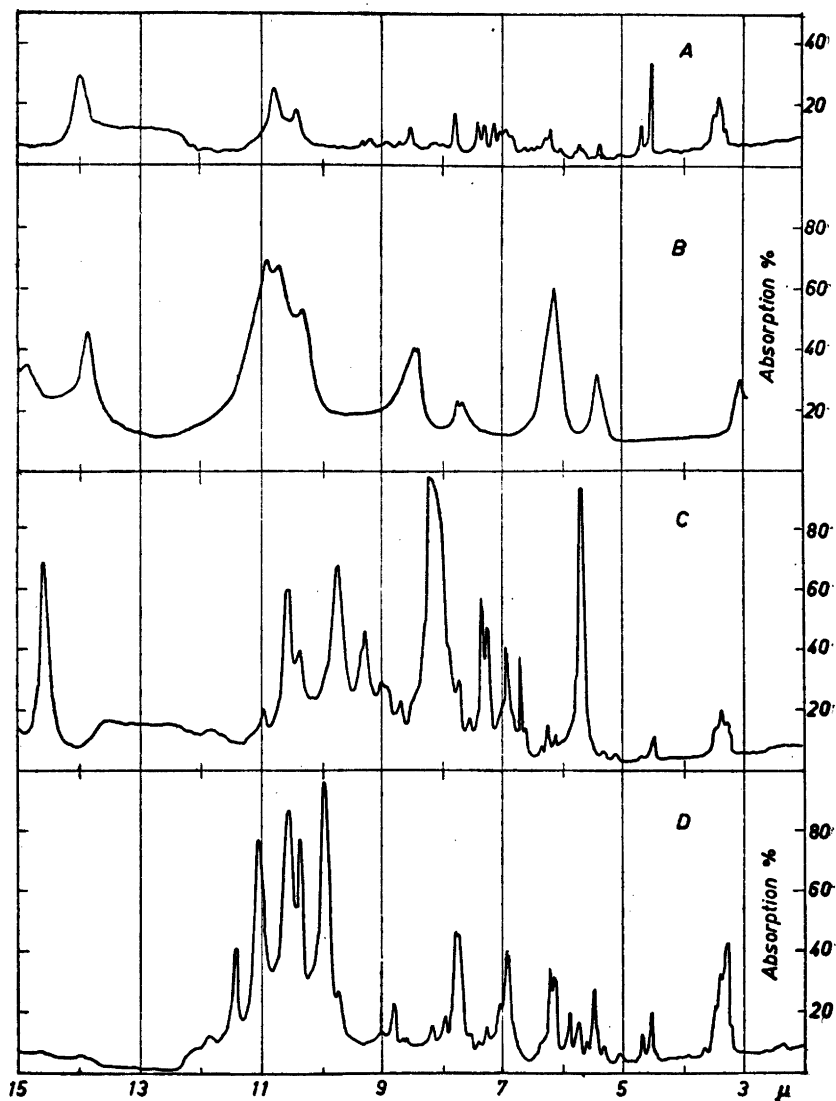


Fig. 2. Infrared absorption of

- A: dodeca-1:11-diene-3:5:7:9-tetrayne (II) in CCl_4 , $c = 7\%$, $l = 0.05$ mm.
 B: divinyl acetylene according to du Pont, 4.25 mol % in N_2 gas, $c = 400$ mm, $l = 10$ cm.
 C: 1-phenyl-hept-5-ene-1:3-diyne-7-yl acetate (V) in CCl_4 , $p = 13\%$, $l = 0.05$ mm.
 D: trideca-1:3:5:11-tetraene-7:9-diyne (IX) in CCl_4 , $c = 19.5\%$, $l = 0.05$ mm.

5–10 % benzene in petroleum ether eluates on slightly deactivated alumina of the essential oil from the following plants: *Carthamus lanatus* L., *Cnicus benedictus* L. and *Silybum Marianum* Gaertn, all three belonging to the tribus *Cynareae*.

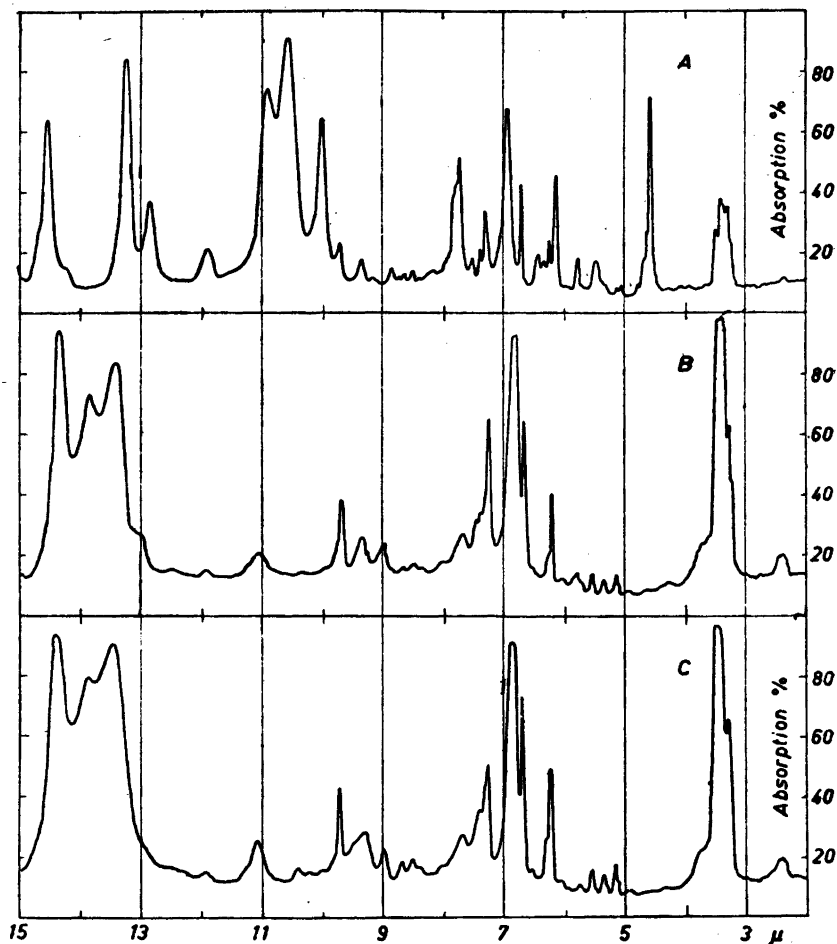
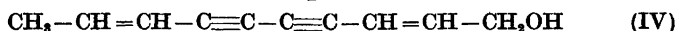


Fig. 3. Infrared absorption of

- A: 1-phenyl-undeca-7:9-diene-1:3:5-triynе (XI), liq. $l = 0.0125$ mm.
 B: 1-Phenyl-*n*-undecane from hydrogenation of (XI), liq. $l = 0.025$ mm.
 C: 1-Phenyl-*n*-undecane synthetic, liq. $l = 0.025$ mm.

We intend to isolate (II) in substance from these *Cynaroideae* as soon as larger samples of the plants are available.

During the chromatographic analysis of the root oil, we have not been able to isolate any pure substance from the eluates with petroleum ether — 10 % benzene until petroleum ether — 70 % benzene. With higher amounts of benzene, sometimes only with pure benzene, there was eluted a substance, which crystallised readily as colourless plates, m.p. 43°, and analysing as $C_{15}H_{12}O_2$. The U.V.-spectrum, Fig. 4, curve A, resembled that of matricarianol¹⁹ (IV), but the first maxima were displaced



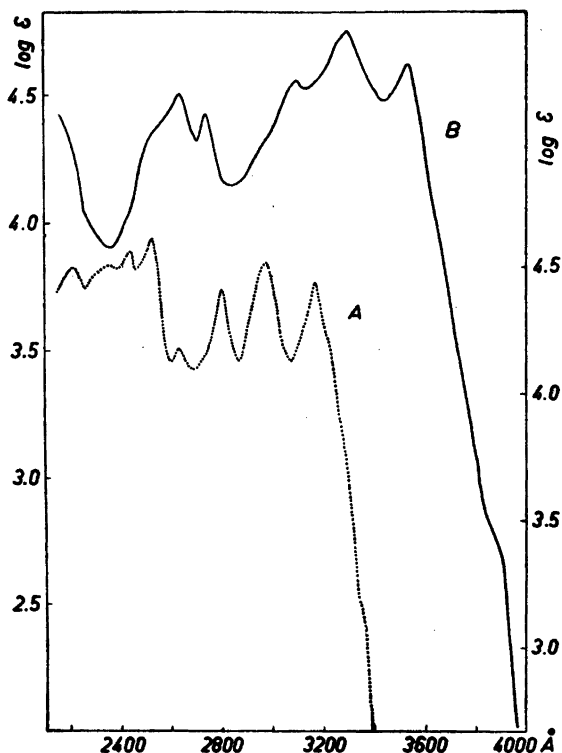
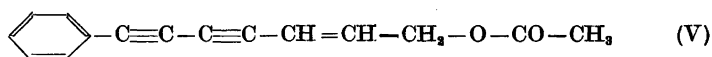


Fig. 4. Ultraviolet absorption in hexane of

- A: 1-phenyl-hept-5-ene-1:3-diyn-7-yl acetate (V), scale left side.
 B: trideca-1:3:5:11-tetraene-7:9-diyne (IX), scale right side.

some 50 ÅU towards longer wave-lengths. The infra-red spectrum of the 43° compound, Fig. 2, curve C, disclosed that the new compound was an ester as indicated by strong peak at 1754 cm^{-1} and a broad and strong band at 1225 cm^{-1} . Moreover, there occurred in the infra-red spectrum a sharp peak at 1490 cm^{-1} , mostly characteristic of phenyl residues. In the U.V.-spectra of polyenes a phenyl group is about equivalent to 1 1/2 double bond¹⁰, whereas in phenyl-poly-yne it has mostly been found equivalent to about one double bond¹¹. The analysis, U.V. and infra-red spectra taken together point to (V) as a reasonable constitutional formula:

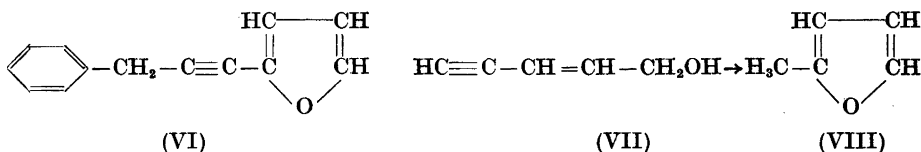


As mentioned in the following communication, (V) was synthesised by Bruun *et al.*¹² by asymmetric Glaser coupling of phenyl-acetylene with pentenyne-ol (VII) to give the free alcohol, m.p. 72–72.5°, which, acetylated with acetic anhydride-pyridine at 0°, furnished (V), m.p. 45–46°, mixed m.p. with the

Coreopsis ester 42—43°. The identity was confirmed by saponification of the natural ester to the free alcohol, m.p. 71—72°, undepressed on admixture with the synthetic compound.

So far most of the polyacetylenic compounds isolated from the *Compositae* have occurred with *cis*-configuration at their double bonds. Since the pentenynol (VII) used in the synthesis of (V) is supposed to be the *trans*-isomer, (V) also must have the *trans* configuration.

Professor E. R. H. Jones and Dr. M. C. Whiting have most kindly pointed out the interesting formal connection between (V) and the "carlina oxide" (VI), one of the first acetylenic compounds which was isolated from an essential oil¹³, viz. that of *Carlina acaulis* L. belonging to *Compositae*, tribus *Cynareae*, subtribus *Carlininae*. Heilbron *et al.*¹⁴ demonstrated the ready conversion of pentenynol (VII) into α -methylfuran (VIII) in acid medium.



The conversion of (V) into (VI) might have proceeded by an analogous mechanism. Several attempts carried out by the Manchester school to realise this transformation have, however, so far been without success.

The crude essential oil from the leaves and stems from the annual *Coreopsis* species showed strong selective absorption in the entire U.V.-region but with rather broad and undistinct maxima. By chromatography on alumina the main part was eluted with the petroleum ether, followed by some small fractions characterised by the presence of the sharp U.V.-maxima of (II). Immediately behind — and in part mixed up with these fractions — there followed, with 5—10 % benzene in petroleum ether, a new compound, responsible for the main U.V.-absorption of the essential oil from the leaves. This compound could be crystallised from petroleum ether at —60° as slightly yellow crystals. These crystals melted at 71—72° and showed very disagreeable properties. Polymerisation to colourless insoluble masses occurred rapidly both in the crystalline state and in solution. In contrast to (II) the 71° compound was oxidised extremely rapidly. The U.V.-spectrum of our best preparations is given in Fig. 4, curve B, the infra-red spectrum in Fig. 2, curve D. The spectra establish the presence of double and triple bonds, but give primarily very little further information.

Catalytic hydrogenation generated a hydrocarbon with the addition of 8 moles of hydrogen which by m.p. —7 to —6°, and mixed m.p. with synthetic tridecane —6.5 to —6°, gave full information about the carbon skeleton. It then remained to arrange 4 double and 2 acetylenic bonds in this normal C₁₃ chain.

Valuable indications about this arrangement were provided by the reaction with maleic anhydride. Although maleic anhydride was used in a large excess the reaction product, m.p. 149—150°, had arisen through addition of only one mole of anhydride. We have not been able to purify

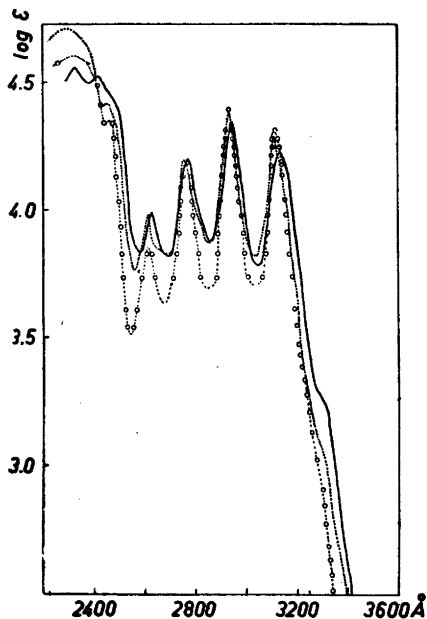
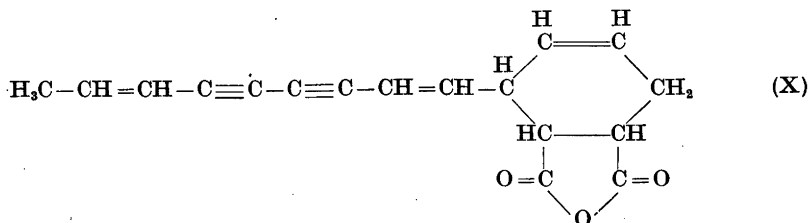
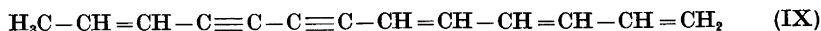


Fig. 5. Ultraviolet absorption in hexane of

— maleic anhydride adduct (X),
 *trans, trans* deca-2:8-diene-4:6-diyne-1-ol (IV),
 -○-○- deca-2:8-diene-4:6-diyne

the adduct to give correct analytical data for $C_{13}H_{12} + C_4H_2O_3 = C_{17}H_{14}O_3$ but during a few preparations of this adduct we unvariably obtained the same U.V.-spectrum, reproduced in Fig. 5 together with the spectra of deca-2:8-diene-4:6-diyne and deca-2:8-diene-4:6-diyne-1-ol = matricaria-nol (IV). The conformity of the 3 curves establishes the maleic anhydride adduct as a derivative of a symmetrical diene-diyne-grouping with alkyl substituents at both ends. It thus follows that the maleic anhydride has been preferentially added into a butadiene end-residue. The 71° compound thus should have the constitution (IX) = trideca-1:3:5:11-tetraene-7:9-diyne with maleic anhydride adduct (X):



Returning to the infrared spectrum of the 71° substance, Fig. 2, curve D, some additional support of formula IX, can be obtained. Curve D has peaks at 905 and 1005 cm^{-1} characteristic of a conjugated vinyl group¹⁵, and at 948 and 966 cm^{-1} characteristic of conjugated and unconjugated *trans* double bonds,

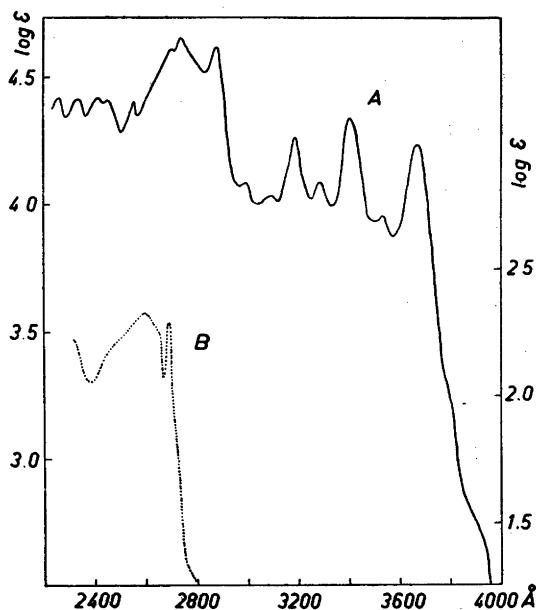


Fig. 6. Ultraviolet absorption in hexane of

- A: 1-phenyl-*n*-undeca-7:9-diene-1:3:5-triyn (XI), scale left side.
 B: 1-phenyl-*n*-undecane from hydrogenation of (XI), scale right side.

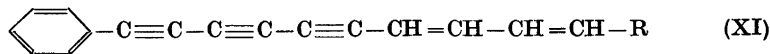
respectively. Since the solvent, CCl_4 , covers most of the region where the *cis* double bond mostly absorb, a *cis* configuration is not excluded, but since the *trans* peaks are strong, most probably all double bonds are *trans*.

The crude essential oil from the flowers of the different annual *Coreopsis* species had also a strong absorption in the entire U.V.-region, but with somewhat more distinct maxima than the oil from the green part. By chromatography on alumina the main part was eluted with the petroleum ether; then followed, with 5–10 % benzene in petroleum ether, fractions which, according to the U.V.-spectra, contained small amounts of the diene-tetraene (II) together with a new substance responsible for the main U.V.-absorption of the flower oils. The separation of this hydrocarbon was somewhat tedious as described in the experimental part. Fig. 6, curve A, gives the U.V.-absorption curve for the main component in hexane. The intersected weak maxima might indicate a mixture of compounds. It should be added, however, that these weak maxima did occur with the same intensities relative to the main maxima in all fractions. After the position of the first maximum at 3 670 Å it has been named the "3 670-hydrocarbon". This hydrocarbon is liquid at room temperature, but can be crystallised from petroleum ether at -70° .

Since it is difficult to get rid of the solvent at low temperatures, no m.p. can be given for the "3 670-hydrocarbon".

The infra-red spectrum, Fig. 3 curve A, indicated, by maxima at 1 600, 1 490, 1 445, 917 and 687 cm^{-1} , that the hydrocarbon contained a phenyl nucleus. This was confirmed by the infra-red spectrum of the product of catalytical hydrogenation (Pd/BaSO₄, Fig. 3, curve B) which, by maxima at 1 610, 1 500, 1 460 and 695 cm^{-1} was characterised as a mono-alkylbenzene. The conclusion was further confirmed by the U.V.-spectrum of this hydrogenation product, Fig. 6 curve B, which agrees perfectly with those of the toluene group¹⁶. The hydrogenation product melted at -8 to $-6,5^\circ$, which comes closest to the data given in literature for 1-phenyl-*n*-undecane, m.p. -5° ¹⁷, -10° ¹⁸, whereas 1-phenyl-*n*-decane has m.p. $-14,4^\circ$ and 1-phenyl-*n*-dodecane has m.p. $+3^\circ$. We have synthesised 1-phenyl-*n*-undecane in different ways, but invariably we have found a m.p. at about -15° for the synthetic phenyl-undecane. The infra-red spectrum of synthetic 1-phenyl-*n*-undecane, Fig. 3, curve C, agreed completely with that of the hydrogenation product. The American Petroleum Institute has no references to the preparation of their standards or to their purification methods, nor do they give any reason for the rather remarkable difference between the published data, nor is any sample of the standards available. The situation is rather unsatisfactory, but as a preliminary working hypothesis we have supposed that the hydrogenation product of the "3 670-hydrocarbon" is 1-phenyl-*n*-undecane; the possibility of polymorphism cannot be excluded.

Additional information about the structure of the "3 670-hydrocarbon" was rendered by the reaction with maleic anhydride. The reaction was very slow, seemed to some extent to be speeded up by illumination of the "3 670-hydrocarbon" before reaction. The adduct crystallised in small spherical aggregates, which decomposed at 146° . The amount of reaction product was not sufficient for analysis but the U.V.-spectrum was very informative, cf. Fig. 7, curve A, where the spectrum of 1-phenyl-octa-1:3:5-triene, the synthesis of which is described in the following communication¹², is given for comparison, curve B. The agreement of the two curves leaves no doubt that the adduct is a derivative of phenyl-triacetylene. Then the "3 670-hydrocarbon" must have the constitutional formula XI



Indications are that R is CH₃. A substitution on the diene system seems very unlikely since the infra-red spectrum, Fig. 3 curve A, has strong peaks at 944 cm^{-1} , characteristic of R-CH=CH-R'. A branching on the diene system should give a hydrogenation product with a significantly lower m.p. The methyl peak in curves A and B, Fig. 3, is scarcely strong enough to account for more than one methyl group, cf. synthetic 1-phenyl-*n*-undecane, Fig. 3 curve C.

We are convinced that still more polyacetylenic compounds could be isolated from the essential oil of *Coreopsis* if chromatographic separation could be performed with somewhat larger amounts of oil. So far some preliminary investigations of other species of the genus *Coreopsis* indicate that further polyacetylenes dominate in other species.

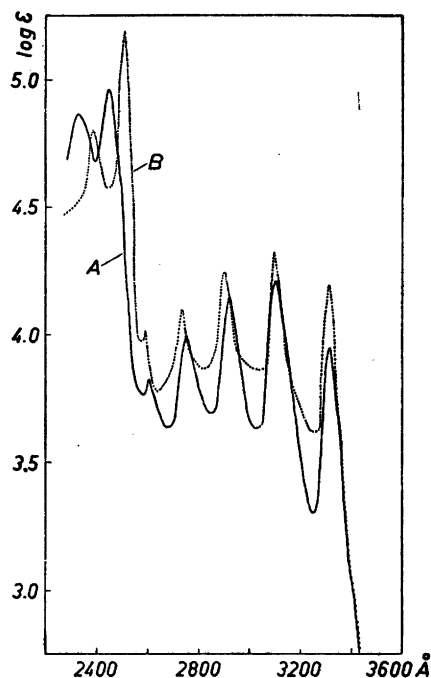


Fig. 7. Ultraviolet absorption in hexane of
 A: maleic anhydride adduct of (XI).
 B: 1-phenyl-octa-1:3:5-triyne.

EXPERIMENTAL PART

The garden varieties of the following *Coreopsis*-species were cultivated at Norges Tekniske Högskole during the season 1952 on seed samples supplied by Norsk Frø A/S, Trondheim, the numbers in brackets refer to the catalogue of that firm: *Coreopsis cardaminifolia* * *atrosanguinea* (3215); *C. Drummondii* (3218); *C. tinctoria* (3221); *C. tinctoria* "nana radiata" (3226); *C. tinctoria* "nigra speciosa" (3229). The material of the perennial *C. verticillata* L. was provided by Mr. R. Persson, Trondheim. As soon as some plants flowered a qualitative investigation was carried out on essential oils prepared from the roots, the stem + the leaves, and from the flowering part of the plants. It was found necessary to carry out the steam distillation with exclusion of light and in a closed system under nitrogen in order to keep decomposition and oxidation at a minimum. For the chromatographical investigation the oils from the different garden varieties were combined according to the agreement of the U.V.-spectra. As adsorbent has been used a slightly deactivated alumina¹⁹.

Root oils

The U.V.-spectra of all the essential oils from the roots of the different varieties and that of *C. verticillata* L. agreed very well and were dominated by the sharp peaks belonging to the diene-tetrayne (II). By the chromatography an appreciable part, mostly about 1/3, went in the first petroleum ether washings. This fraction was a colourless liquid with selective absorption below 2600 ÅU only, and might consist of terpene hydrocarbons.

The last washings with petroleum ether and the first eluates with 5 % benzene, which together accounted for only 3 % of the oil, contained all the diene-tetrayne (II). These fractions from the different varieties were combined and rechromatographed until no further change in the U.V.-absorption curve. From petroleum ether these fractions deposited slightly yellow crystals when stored at -15° for some hours. The crystals were

washed with petroleum ether at -15° and dried by evacuation at the oil pump at room temperature. In a sealed m.p. tube the crystals became discoloured from 43° and turned black at about 47° with no further change until 200° .

U.V.-spectrum in hexane, Fig. 1, curve A.

ϵ_{\max}	13 400	20 900	17 200	11 650	143 000	189 000	143 000
λ_{\max}	3 905	3 610	3 370	3 155	2 875	2 710	2 580 ÅU
$\Delta\nu_{\max} \cdot 10^{-12}$	62.8	59.2	60.7				

Infra-red spectrum Fig. 2, curve A.

Catalytical hydrogenation. 4.44 mg was hydrogenated in alcoholic solution with 31.3 mg catalyst. Consumed (21° C, 740 mm) 7.58 ml, calculated for $C_{12}H_{24}$, $4/3$, $2/3 = 7.52$ ml. The hydrogenation product was isolated in the usual way and distilled at 0.3 mm, 40° air bath temperature. The distilled hydrocarbon crystallised readily below -15° and melted sharply between -10.8 and -10.3° . For comparison *n*-dodecane was prepared by catalytical hydrogenation of pure lauryl bromide with Pd/CaCO₃-catalyst and melted at -10 to -9.3° , given in literature -9.6° . Mixed m.p. of equal amounts of the hydrogenation product and synthetic dodecane -12.3 to -11.5° .

Reaction with peracetic acid: 6.6 mg of (II) was dissolved in the calculated amount of 10 % peracetic acid and left at room temperature for 2 days. A U.V.-spectrum revealed that practically no reaction had taken place. 2.6 mg of crystalline (II) was then dissolved in 2 ml of 10 % peracetic acid. After 24 hours at room temperature the characteristic spectrum of (II) had been displaced by new sharp maxima at 2 450, 2 330, 2 235 ÅU. Dialkyl-tetraynes⁴: 2 410, 2 300, 2 200 ÅU.

With 10 % benzene in petroleum ether until 70 % benzene in petroleum ether some fractions were eluted, which together amounted to about 10 % of the oil, and showed undistinct and variable U.V.-spectra. Since each fraction was small and the spectra agreed with corresponding fractions from flower and leave oils they have not been investigated any further.

When the percentage of benzene was raised above 70 %, about 30 % of the starting material was eluted which readily deposited small amounts of colourless plates from petroleum ether in the cold. Since the total eluates showed only a broad step out in U.V., the mother liquor should contain a mixture of chromophores mainly with short-waved selective absorption. After some recrystallisations the colourless plates melted constantly at 43° . (Analysis: *Micro-analytische afdeling, Laboratorium v. Org. Scheikunde der Universiteit v. Amsterdam*. Found: C 79.8; H 5.6. Calc. for $C_{15}H_{12}O_2$ (224.2): C 80.3; H 5.39).

Ultraviolet absorption spectrum in hexane; cf. Fig. 4.

ϵ_{\max}	27 600	32 400	25 700	15 200	40 800	37 200	32 000
λ_{\max}	3 175	2 980	2 810	2 630	2 530	2 450	2 220 ÅU
$\Delta\nu_{\max} \cdot 10^{-12}$	61.8	60.9	73.1				

Infra-red spectrum in carbon tetrachloride, cf. Fig. 2 curve C.

A 1:1 mixture with synthetic (V), m. p. $45-46^{\circ}$ ¹² melted at $42-43^{\circ}$.

Saponification: Some mg of not quite pure 43° -ester was saponified at room temperature under nitrogen with aqueous alkali with addition of acetone until the solution was homogeneous. After 1 hour the saponification mixture was worked up. The chromophore was obtained in the unsaponifiable part which in the crude state was a red oil. This oil was distilled at 0.001 mm and 90° air bath temperature and the distillate recrystallised twice from petroleum ether; colourless crystals, m.p. $71-72^{\circ}$, synthetic 1-phenylhept-5-ene-1:3-diyn-7-ol $72-72.5^{\circ}$ mixed m. p. $71-72^{\circ}$.

The amount of essential oil from the *green part* of the plants amounted to some grammes from each of the garden varieties and therefore the chromatographic separation was carried out with each single variety. The results of the different runs were in very good agreement.

About 3/4 of the oil went in the first washings with petroleum ether and consisted of a colourless oil with U.V.-maximum at 2 280 ÅU (natural farnesene).

With 10 % benzene in petroleum ether the main chromophore of the oil from the green parts was eluted. These crude fractions amounted to some 3 % of the starting material and mostly left a crystalline residue by evaporation *in vacuo*. Recrystallisation from petroleum ether afforded yellow needles, m. p. 71–72°.

U.V.-absorption spectrum in hexane, Fig. 4.

ϵ max	42 200	57 200	36 000	26 700	32 000
λ max	3 535	3 300	3 100	2 470	2 640 ÅU
$\Delta\nu$ max. 10^{-12}	60.4	57.6			

Infra-red spectrum in carbon tetrachloride solution, Fig. 2, curve D. At an air bath temperature of 68–70° this hydrocarbon can be distilled slowly at 0.0001 mm; if the temperature exceeds 75° decomposition takes place.

Catalytical hydrogenation: 54.2 mg was hydrogenated in alcoholic solution with Pd/BaSO₄-catalyst. C₁₃H₂₆, 2/≡, 4/≡ calc. 19°, 750 mm 64.0 ml H₂, observed 65 ml H₂.

The hydrogenation product was isolated in the usual way and distilled at 0.3 mm and 50° air bath temperature. The distillate crystallised readily in the refrigerator and then melted at –7 to –6° C.

For comparison *n*-tridecane was synthesised from *n*-tridecan-4-ol synthesised by Grignard reaction of *n*-propyl bromide with *n*-decylaldehyde. The *n*-tridecan-4-ol was recrystallised from dilute alcohol in the refrigerator and distilled at 0.3 mm. n_D^{20} obs = 1.48325, given²² is 1.483. The *n*-tridecan-4-ol was dehydrated with KHSO₄ + K₂SO₄ at 170° for 5 hours and the olefin isolated in the usual way and distilled over a little sodium metal. 1.14 g of tridecene was hydrogenated with Pd/BaSO₄ catalyst in alcohol solution, C₁₃H₂₆, 1/≡ calc. 144 ml at $t = 21^\circ$ and 754 mm H₂, consumed 135 ml. The hydrogenation product, *n*-tridecane was isolated in the usual way and distilled. The distillate melted at –6 to –5.8°, given in literature²¹ –5.3°. Mixed m. p., synthetic *n*-tridecane with the hydrogenation product from the 71° hydrocarbon from *Coreopsis*, at –6.5 to –6°. For comparison a mixed m. p. determination was carried out also between synthetic dodecane, m. p. –10 to –9.3°, and the hydrogenation product from *Coreopsis*, m. p. –7 to –6; a 1:1 mixture melted unsharply at –13 to –11.5° C, *i. e.* with a definite depression of the lower m. p.

Reaction with maleic anhydride: 120 mg of the 71°-substance was dissolved in a few ml benzene and a great excess (~ 2 g) of maleic anhydride was added and the solution sealed up under pure nitrogen and heated for 1 hour at 60–65° C. The reaction mixture was evaporated, the solvent at 15 mm, the excess maleic anhydride at 0.0001 mm, air bath at 40° C. The solid residue was dissolved in benzene and after addition of petroleum ether left in the refrigerator. After 24 hours the solutions had deposited colourless needles, m. p. 146–148°. Recrystallisation from benzene-petroleum ether 1:1 raised the m. p. to 149–150° C. Found: C 75.2, 75.8; H 5.1, 5.5. Calc. for C₁₃H₁₂ + C₄H₂O₃ = C₁₇H₁₄O₃: C 76.6; H 5.3. Calc. for C₁₂H₁₀ + C₄H₂O₃ = C₁₆H₁₂O₃: C 76.1; H 4.8. The C-values thus indicated C₁₂H₁₀ which had been excluded by the catalytical hydrogenation. The adduct decomposed readily and for this reason was difficult to analyse.

U.V.-spectrum in hexane, Fig. 5, curve A.

ϵ max	16 800	22 200	16 000	9 900	33 600	36 000
λ max	3 135	2 940	2 770	2 630	2 420	2 330 ÅU
$\Delta\nu$ max. 10^{-12}	63.5	62.6	57.7			

The chromatographic column was eluted further with increasing concentrations of benzene in petroleum ether. The fractions eluted were small and with undistinct spectra. Benzene eluted strongly coloured yellow fractions which from petroleum ether deposited the colourless plates of (V) m. p. 42.5 undepressed by (V) from the root oil.

Flower oils

By the chromatography of the essential oil from the flowers the main part — about 2/3 — also was eluted with the first petroleum ether fractions and, like the corresponding fractions from the leaves, seemed to consist of terpene hydrocarbons. With a few per cent benzene in petroleum ether some fractions were eluted, totalling about 10 % of the starting material, which according to spectroscopical U.V.-evidence contained mixtures of the diene-tetraene (II) and the "3 670-hydrocarbon". We tried to separate this mixture by distillation at 0.0001 mm, but the distillate obtained at a bath temperature of 50° was small and, according to the U.V.-spectrum, seemed to contain the same mixture of the two hydrocarbons. The residue decomposed.

The best method appeared to be rechromatography on deactivated alumina with large amounts of petroleum ether followed by a mixture of 1 % benzene in petroleum ether. The fractions devoid of the 3 915 peak characteristic of (II) were redistilled, boiling range 50–60° at 0.0001 mm.

Ultraviolet absorption in hexane, Fig. 6, curve A.

ϵ_{\max}	17 100 (8 800)	21 600 (12 000)	18 400 (10 800)	12 400	41 200	45 200
λ_{\max}	3 670 (3 525)	3 405 (3 285)	3 186 (3 095)	2 990	2 875	2 735 ÅU
$\Delta\nu_{\max} \cdot 10^{-12}$	63.7		60.5	61.7		
	62.1		56.1			

Infra-red absorption, liq., Fig. 3, curve A.

Catalytical hydrogenation: 183 mg of freshly distilled "3 670-hydrocarbon" was checked spectrographically in hexane solution, the hexane solution concentrated and added to freshly prepared Pd/BaSO₄ catalyst in alcohol. The consumption of H₂, 8.5 moles, was somewhat in excess of the amount calculated for C₁₇H₁₂, 3/≡, 2/≡.

The hydrogenation product was isolated in the usual way and distilled at 0.0001 and 35° air bath temperature, m. p. —10 to —9°. It could be crystallised from petroleum ether at —70°. The recrystallised hydrocarbon melted at —8 to —6.5° C. Infra-red spectrum, Fig. 3, curve B. U.V.-spectrum, Fig. 6, curve B.

Maleic anhydride adduct. About 10 mg of "3 670-hydrocarbon" was diluted with pure benzene and the benzene solution saturated with maleic anhydride, sealed up in a glass tube under pure nitrogen and heated to 40°. The bath temperature was raised slowly to 70° during 4 hours. The solvent was evaporated and the large excess of maleic anhydride sublimed off at 40° and 0.001 mm. The residue was dissolved in petroleum ether. In the refrigerator this solution deposited small spherical clusters with decomposition point 146°.

U.V.-spectrum, Fig. 7, curve A.

ϵ_{\max}	9 060	16 500	13 700	9 620	6 570	91 700	72 800
λ_{\max}	3 317	3 105	2 920	2 750	2 605	2 450	2 327 ÅU

During chromatography of the oil from the flowers the "3 670 fractions" were immediately followed by fractions containing the trideca-1:3:5:11-tetraene-7:9-diyne (IX), m. p. and U.V.-spectra. With 50 to 70 % benzene in petroleum ether there followed some liquid, orange-red fractions amounting to 1–2 % of the starting material with very undistinct spectra in both visible and U.V.-regions. We have not been able to separate this fraction into pure compounds.

Pure benzene eluated about 1 % of the starting material as semisolid coloured fractions, which by crystallisation from petroleum ether afforded the colourless leaflets of (V) m. p. 43°.

Coreopsis verticillata L. A few flowering plants of this species were bought from Mr. R. Persson, Trondheim, to obtain a preliminary insight into a perennial *Coreopsis* species. The flowers (29 g) gave 1 % of essential oil with only very weak and undistinctive absorption in U. V.

The leaves and stems (215 g) gave 0.4 ‰ of essential oil with rather strong selective absorption in U. V., maxima at 3 100, 2 963 and 2 830 ÅU. The positions of these maxima as well as the general trend of the U.V.-absorption curve were in excellent agreement with those of cosmene = 2:6-dimethylocta-1:3:5:7-tetraene¹⁵. The concentration of cosmene in the essential oil of *C. verticillata* amounted to 17 %.

The roots (120 g) gave 0.4 ‰ of essential oil with a U.V.-spectrum composed of the very characteristic maxima of II and those of cosmene. The calculated content of dodeca-1:11-diene-3:5:7:9-tetraene II was very small, 1.6 %, whereas cosmene amounted to 20 % of this essential oil.

Carthamus lanatus L. We are indebted to professor dr. Rolf Nordhagen, director of the Botanical Garden at the University of Oslo, for small samples of the investigated thistles. Mr. F. E. Eckblad, assistant at the University Botanical Garden, had the kindness to dry the plants at ordinary temperature and in absence of light. The sample of *C. lanatus* L. was so small that a division of the plants in the main parts had to be abandoned. The essential oil of the whole plant had a broad and complex absorption in U.V. By chromatography on alumina the petroleum ether washings brought out a small fraction (1.4 mg) with the very distinct maxima of dodeca-1:11-diene-3:5:7:9-tetraene (II). The calculated content of (II) in this small fraction was — 3 %. With about 20 % benzene in petroleum ether there was eluted a chromophore with an extremely complex U.V.-spectrum resembling some phenanthrene-spectra. Our hydrocarbon which possesses first maxima at 3 550, 3 335 and 3 180 ÅU, has been found in small amounts in some other plants of the Compositae.

Cnicus benedictus L. The starting material was a few dried plants from the University Botanical Garden in Oslo, cf. above. The material was practically devoid of roots and was steam distilled without separation. The essential oil had a strong absorption in the entire U.V.-region with several small peaks. Chromatography on alumina disclosed that this oil consisted of a very complicated mixture. With 2 % benzene in the petroleum ether there was eluted a fraction (12.9 mg) with the very distinct spectrum of (II), calculated concentration 0.4 % 20 % benzene in petroleum ether eluted the same hydrocarbon, maxima at 3 550, 3 335 and 3 180 as with *Carthamus*. None of the fractions contained enough substance to permit preparative work.

Silybium Marianum Gaertn., starting material a few dried plants from the University Botanical Garden of Oslo cf. above. The small amounts of roots were extracted with acetone, the small quantity of extract (5.7 mg) showed only a step out below 3 000 ÅU.

The rest of the plants were distilled with steam, to give an oil which had a broad and rather undistinct absorption in U. V. By chromatography on alumina the oil was split up into a number of fractions, which according to the U.V.-spectra mostly still should be rather complex mixtures. The fraction eluted with 10 % benzene, however, had an U.V.-absorption conform with the standard curve for II; the content of (II) in this fraction amounted to only 1 ‰.

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