

Studies Related to Naturally Occurring Acetylene Compounds

XXXIII. A Preliminary Investigation of *Coreopsis gigantea*

(Kell.) H. M. Hall

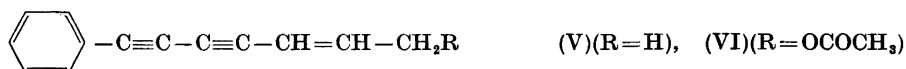
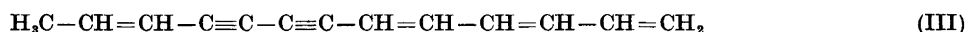
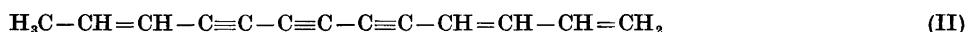
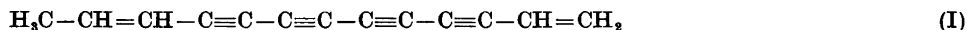
JØRGINE STENE SØRENSEN and NILS ANDREAS SØRENSEN

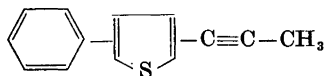
Institutt for organisk kjemi, Norges tekniske høgskole, Trondheim, Norway

The lower stem and root of *Coreopsis gigantea* (Kell.) H. M. Hall contain anol isovalerate (D = XVII) and three acetylenes with ene-diyne-diene chromophores as principal components. A hydrocarbon (A) must be closely related to the C₁₇-acetylene Centaur X₄ (XII). An acetate (B) is shown to be the C₁₄-compound (XIII). The fourth acetylenic compound (C) is shown to be a C₁₇-compound (XVI), that is a hydroxycompound of A.

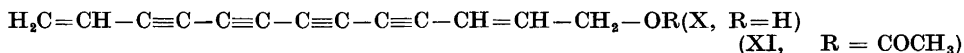
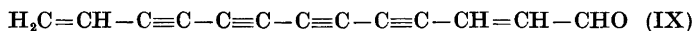
No one of the eleven C₁₃-acetylenes found earlier in the genus *Coreopsis* could be traced. The three acetylenic compounds present in *C. gigantea* are very closely related to acetylenes found in botanically distant members of the *Compositae*.

The genus *Coreopsis* comprises 114 species, according to the monograph of E. E. Sherff.¹ Sherff divides the genus into 11 sections, most of these sections having been given genera rank by earlier taxonomists. About a dozen species of *Coreopsis* have been investigated on the occurrence of acetylenic compounds,²⁻⁷ and the following eleven more or less closely related acetylenes have been described:





(VIII)



Most of the species investigated belong to the two sections *Eucoreopsis* Nutt. and *Calliopsis* (Reichenb.) Nutt. Only scattered representatives of *Eublepharis* Nutt., *Euleptosyne* (A. Gray) Blake and *Pugiopappus* (A. Gray) Blake, have been investigated.

In connection with previous investigations of some *Coreopsis* species on the occurrence of XI, cf. Ref. 6, we also examined material from so called *C. maritima* (Nutt.) Hook, belonging to the section *Tuckermannia* (Nutt.) Blake. The plants had been grown from seeds supplied by different European botanical gardens, and the fully developed plants showed close similarity.

While visiting Los Angeles we were introduced, by Professor T. A. Geissman, to the second member of the genus *Tuckermannia*, viz. *C. gigantea* (Kell.) H. M. Hall. Professor Geissman's studies of the aurone pigments of different *Coreopsis* flowers are well known.^{8,9}

Morphologically *C. gigantea* differed sharply from all *Coreopsis* species investigated by us and when we compared the differences between *C. maritima* and *C. gigantea* in Sherff's monograph we became suspicious about the earlier investigated material of *C. maritima*. With the generous assistance of Professor Geissman, a chemical investigation of genuine *C. gigantea* was made possible. Because of air transport problems the investigation has been restricted to the lower part of the strong stem and the main part of the root of *C. gigantea*.

Extracts of *C. gigantea* contain four main chromophoric substances, a hydrocarbon (A), an acetate (B), and an alcohol (C) having almost identical UV-spectra corresponding to an ene-diyne-diene-chromophore. The fourth compound (D) has a single and broadbanded chromophore, UV maximum 2530 Å, where the UV-spectrum alone leads to no definite conclusion.

The extracts were separated in the usual way by chromatography on deactivated alumina. The least polar ene-diyne-diene-component (A) was closely accompanied by one (D) containing a system showing a broadbanded absorption at 2530 Å. Repeated, careful re-chromatography was necessary in order to isolate the non-polar ene-diyne-diene-compound. UV-spectroscopy was not very helpful, but as the 2530-substance (D) at an early stage of fractionation was recognized as a carbonyl compound with a sharp IR-band at 1768 cm⁻¹, the separation could be controlled by IR-spectroscopy.

Hydrocarbon A. The non-polar ene-diyne-diene (A), crystallised from petroleum ether, had a melting point of 29°C.

The IR-spectrum of the pure substance (A) indicated a vinyl group (1830, 908 cm⁻¹). A strong band at 983 cm⁻¹ pointed to a *trans*-diene-chromophore beside the vinyl and another strong band at 940 cm⁻¹ to a single *trans* ethylenic bond. As was to be expected from the definite ene-diyne-diene chromophore seen in the UV-region, the acetylene region (2100–2250 cm⁻¹) had 2 bands

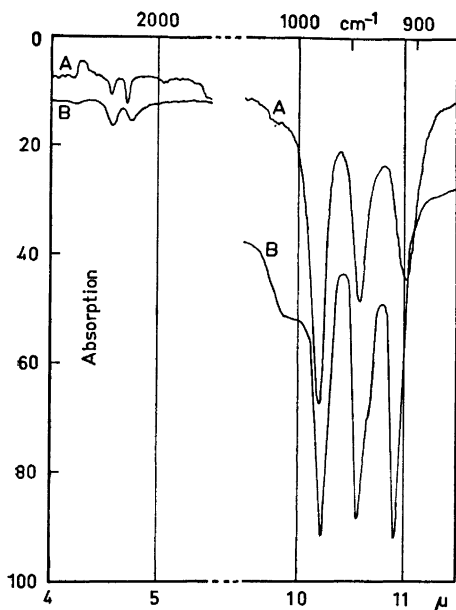


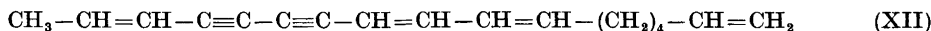
Fig. 1. Critical parts of the infrared spectra. A: Hydrocarbon (A) from *Coreopsis gigantea*, this work; B: Centaur X₄ (XII) from *Centaurea ruthenica*, Bohlmann *et al.*¹⁰

at 2200 and 2125 cm⁻¹; the unusual thing being however, that the intensity of the 2125 cm⁻¹ peak exceeded that of the 2200 cm⁻¹ peak; *cf.* Fig. 1.

By catalytic hydrogenation heptadecane was produced, the identification being effected by gas chromatography and mixed melting point determinations.

As a *trans* diene this hydrocarbon readily adds on maleic anhydride, the adduct having a melting point of 122–124°C, and as might be expected, a definite ene-diyne chromophore in the UV-region.

The Centaur X₄ hydrocarbon isolated by Bohlmann, Postulka and Ruhnke¹⁰ from *Centaurea ruthenica* Lam, has a melting point of 27–29°C, and the diene adduct one of 119°C. Bohlmann *et al.* give the structure XII.



The hydrocarbon XII and (A) are obviously very similar; the IR-spectrum of XII given in Ref. 10 differs, however, both in the relative intensity of the 10–11 μ bands and in the relative peak heights of the acetylene bands, the 2200 cm⁻¹ band in Centaur X₄ being, as is usual in polyacetylenes, stronger than the side band; *cf.* again Fig. 1.

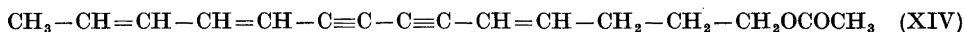
The synthesis of appropriate model substances is obviously necessary to establish the difference between hydrocarbon A and Centaur X₄. The unusual intensity relation between the 2200 and 2125 cm⁻¹ bands has been met in some few other cases studied in this laboratory, but we have not so far been able to deduce the structural detail responsible for its occurrence.

Acetate B. The second acetylenic component (B) was eluted with benzene:petroleum ether 1:1. The UV-spectrum of this fraction remains unchanged showing ene-diyne-diene absorption. After several recrystallisations from petroleum ether at –20°C, the substance had a melting point of 31–33°C.

Infrared evidence reveals that substance B is an acetate ester (1740, 1385, 1220, 1042 cm^{-1}). Otherwise its spectrum shows general agreement with the IR-bands of the ene-diyne-diene-hydrocarbon (A), and in particular with the strong acetylenic band at 2128 cm^{-1} .

Saponification gave rise to an alcohol (m.p. 103–104°C). In the spectrum of this alcohol the unusual intensity relation between the acetylene peaks is retained. The new hydroxyl band at 1052 cm^{-1} indicates a primary alcohol in non-allylic position. The evidence for this conclusion was strengthened by the recovery of the alcohol unchanged after treatment with active manganese dioxide.¹¹ During catalytical hydrogenation, 6.5 moles of hydrogen were taken up. The perhydro alcohol was distilled and crystallised from petroleum ether and these crystals had a melting point of 35.1–35.5°C and a mixed melting point with authentic tetradecanol at 35.7–36.1°C. The identity was confirmed by gas chromatography.

From the above-ground part of *Anthemis carpatica* Willd., Bohlmann, Bornowski and Arndt¹² isolated, as a minor component, a liquid acetate with a diene-diyne-ene chromophore. The corresponding alcohol melted at 99–100°C. Of the two possible structures XIII and XIV:

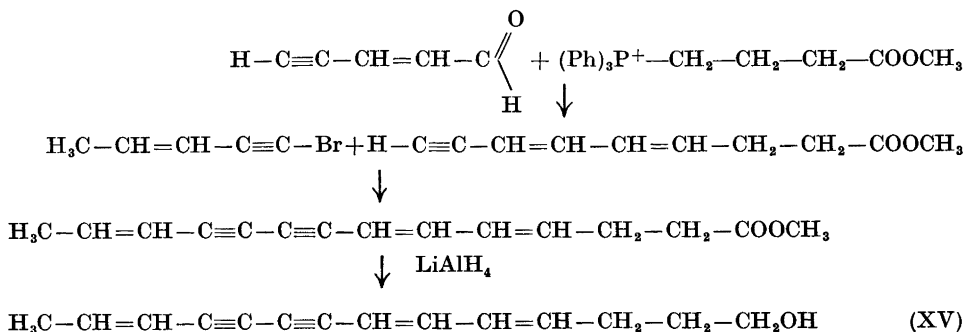


Bohlmann *et al.* preferred XIII because the type XIV has so far not been isolated from plant products.

Bohlmann *et al.*¹² have given only the position of some few IR bands of their acetate and the corresponding alcohol, and no data on the relative intensities of the acetylenic bands. The abnormality of these would have revealed the possible identity of the two substances occurring in two tribes of the *Compositae* (*Anthemideae* and *Heliantheae*). These mostly contain rather different acetylenes.

The structure XIII, given for the *C. gigantea*-substance, was proved to be correct by the following synthesis.

The synthesis is described in detail in the experimental part of this paper. The difficult point is, as usual, the *cis-trans* mixture from the Wittig-Schoellkopf-synthesis. The melting point of the pure alcohol XV could, after some recrystallizations and vacuum sublimations, be raised to 106°C. No depression



of melting point was observed when mixed melting point determinations were done with the saponification product of the *Coreopsis*-acetate (B). The agreement of the infrared spectra of synthetic XV and the alcohol from acetate B was complete, the intensity of the 2128 cm^{-1} peak being stronger than that of the 2200 cm^{-1} .

As mentioned above, Bohlmann *et al.*¹¹ first isolated the acetate XIII from *Anthemis carpatica*. After this investigation was completed, Bohlmann and Kleine¹⁶ re-isolated XIII from *Dahlia Merckii* Lehm., together with the free alcohol (XV). The melting point of the alcohol (XV) was given as $110\text{--}111^\circ\text{C}$ and from XV the acetate was obtained in crystalline form (m.p. 31°C). This was in excellent agreement with the material from substance B from *Coreopsis gigantea*. No curves are given for the infrared spectra, only the position of the main bands. Bohlmann and Kleine briefly mention that they have isolated XIII also from *Cotula coronopifolia* L. and *Coreopsis coronata* Hook. Our own investigations of some members of the genus *Cotula* will be given in next following communication in this series. In our Australian material of *C. coronopifolia* the acetate (XIII) dominated over the free alcohol (XV).

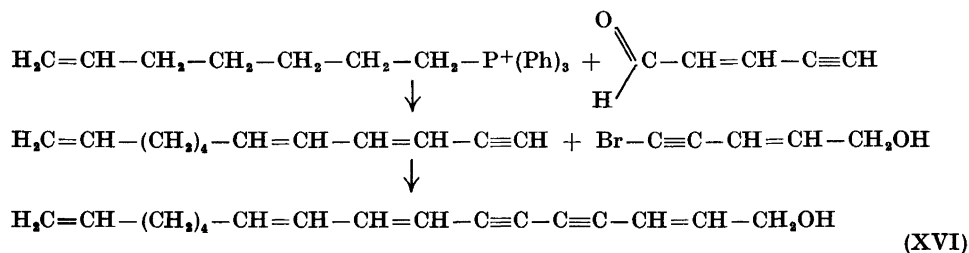
The observation, by Bohlmann and Kleine of XIII in *Coreopsis coronata* Hook (designated *C. nuccensis* Heller by Sherff¹), is interesting. This species belongs to section VII, *Eucoreopsis*, where so far only substances with a chain-length of C_{13} have been observed.

Alcohol C. On the alumina column there occurred a grey-green band of decomposed chlorophyll. Just after this band there was eluted a third enediyne-diene chromophore. The substance crystallized well from petroleum ether and had a melting point of $75\text{--}76^\circ\text{C}$.

IR-spectroscopy revealed that this substance was a free alcohol. The OH-bands at 1088 and 1032 cm^{-1} indicated a primary and allylic alcohol function.¹³ This was confirmed by smooth oxidation, with active manganese dioxide, to a conjugated aldehyde, (maximum at 3680 \AA). The carbonyl frequency of this aldehyde is at 1118 cm^{-1} indicating an yn-ene-al grouping. The dien-al grouping exhibits absorption at 1100 cm^{-1} and the yn-al grouping at 1170 cm^{-1} .

The IR-spectrum further contains two acetylenic bands at 2200 and 2125 cm^{-1} with normal intensity relation. A band at 946 cm^{-1} indicates *trans* ene, and a strong band at 987 cm^{-1} a conjugated *trans* diene. Vinyl grouping is seen at 3100 , 1840 and 910 cm^{-1} .

The chain length was determined by catalytic hydrogenation to heptadecanol. Together with the spectroscopic evidence this indicates the constitutional formula XVI. This was confirmed by the following synthesis:



Bidens, the present results suggest two courses of investigation. Firstly an examination is required of all parts of *C. gigantea*. This very showy plant grows between San Louis Obispo and Ventura County, S. W. California, in sand-dunes under very special climatic conditions and our attempts to cultivate this plant in greenhouses in Trondheim have met with very little success as the plants wilted quickly. Secondly the discovery of the four compounds in *C. gigantea* calls for further investigation of members of this large genus, especially from the less known sections.

EXPERIMENTAL

Professor T. A. Geissman very kindly arranged the collection of 7 lbs. of the roots and adjacent lower stem parts of *C. gigantea*. The material was immediately sent by air to Trondheim where it was cut into thin slices and extracted with acetone. The acetone extracts were transferred to petroleum ether, washed free of acetone, dried and chromatographed on alumina.

S u b s t a n c e A

The petroleum ether filtrate showed a distinct diene-diyn-ene spectrum. The fractions with the highest extinction values were bulked. All these fractions gave a rather strong 1770 cm^{-1} peak in the IR region. By careful re-chromatography on alumina a separation of the hydrocarbon A from the ester D was successful in so far as one fraction of A was obtained free of the 1770 cm^{-1} peak; all the fractions enriched in D still contained the hydrocarbon A.

The ester-free fraction was concentrated and crystals formed at -20°C (m.p. 25°C ; after re-crystallisation 29°C , UV-spectrum in petroleum ether confirmed the diene-diyn-ene chromophore¹⁴). The IR-spectrum was in complete agreement with that of Centaur X₄¹⁰ with the exception of the intensity differences demonstrated in Fig. 1.

Catalytic hydrogenation. 55 mg was hydrogenated in alcohol with palladium, 41 ml hydrogen was consumed; calculated for 8 carbon-carbon double bonds (C₁₇H₂₀) 45 ml. The perhydrogenation product was distilled at 0.01 mm Hg. Colourless plates formed (m.p. $22,5-23^{\circ}\text{C}$).

Analytical gas chromatography with hexadecane to octadecane as comparison compounds definitely proved the perhydrogenation product to be heptadecane.

Maleic anhydride adduct. To 0.7 g freshly sublimed maleic anhydride dissolved in benzene about 50 mg A was added. The solution turned yellow and was stored for 24 h; the solvent and excess maleic anhydride were removed in high vacuum, and the residue was crystallised from petroleum ether. The melting point was $122-124^{\circ}\text{C}$.

UV maxima 2820, 2670, 2530, 2400, 2290, 2130 Å were characteristic of ene-diynes.

S u b s t a n c e B

On the main chromatography on alumina a second compound with diene-diyn-ene chromophore was eluted with petroleum ether, benzene (1:1). The crude fraction was coloured deep green by chlorophyll decomposition products. With some difficulty colourless crystals could be obtained by repeated crystallisations from petroleum ether. The first crystals had a melting point of $29-30^{\circ}\text{C}$. This was raised by further crystallisation to $31-33^{\circ}\text{C}$.

The UV-spectrum of B conforms with that of A and known diene-diyn-enes.¹⁴ The IR-spectrum on the molten substance B is as follows: acetate ($1740, 1363$, and 1220 cm^{-1}), CH₃ (1385 cm^{-1}), *trans* diene 983 cm^{-1} , *trans* ene 948 cm^{-1} , acetylene peaks 2200 and 2128 cm^{-1} , the 2200 cm^{-1} peak is about 60 % the intensity of the 2128 cm^{-1} peak.

Saponification of B gave an alcohol (m.p. $103-104^{\circ}\text{C}$) with unchanged diene-diyn-ene chromophore. In the IR-spectrum the unusual intensity relations between the acetylene peaks are retained, a new band at 1052 cm^{-1} indicates a primary alcohol in non-allylic

position. The alcohol was recovered unchanged after 18 h shaking with active manganese dioxide at room temperature.

The alcohol was hydrogenated in alcohol solution with palladium as above. The perhydrogenation product was isolated as usual and distilled and the entire distillate crystallised (m.p. 35.0–35.5°C, no melting point depression with n-tetradecanol). Analytical gas chromatography with tetradecanol and hexadecanol as comparison alcohols established the perhydrogenation product as tetradecanol.

Synthesis of tetradeca-4,6,12-triene-8,10-diynol (XV). Pent-2-ene-4-yn-ol-1 was prepared by oxidation of pent-2-ene-4-yn-ol-1 with active manganese dioxide.

All efforts to produce the triphenylphosphonium salt from methyl- γ -bromo-butyrates in the standard solvent ether were completely unsuccessful because of side reactions. After some model experiments with different solvents, *viz.* without solvent, it was found that this type of alkylhalogenid gave a reasonable yield of phosphonium salt at 70°C by use of the same amount of dry benzene as alkyl bromide. 5 g methyl- γ -bromobutyrate and 7.5 g triphenylphosphine in 5 ml dry benzene was kept for 4 days at 70°C. The yield was 8.3 g phosphonium salt (m.p. 177–178°C).

Methyl-nona-4,6-dien-8-yn-oate-1. All efforts to prepare the ylid from the triphenylphosphonium salt of methyl- γ -bromobutyrate were in vain. Successive generation of the ylid in the presence of pentynal under the conditions specified finally led to a smooth reaction but also to a typical *cis-trans* mixture.

5.5 g phosphonium salt from methyl- γ -bromobutyrate (m.p. 178°C) and 0.5 g pent-2-en-4-yn-ol-1 dissolved in 50 ml dry tetrahydrofuran was warmed until gentle boiling, the condenser being sealed with soda lime. A solution of 0.3 g sodium in 8 ml absolute alcohol diluted with 50 ml dry tetrahydrofuran was added slowly under stirring. When after 3/4 h the addition was completed the reaction was interrupted by addition of water (40 ml). The clear solution was extracted with ether, worked up as usual and distilled (90°C air bath, 0.3 mm. Hg).

The UV-spectrum exhibited a maximum at 2620 Å with a definite shoulder at 2715 Å.

The IR-spectrum showed free acetylene at 3310 and 2100 cm^{-1} , ester at 1735 and 1170 cm^{-1} , conjugated *trans* diene at 985 cm^{-1} and a strong band at 938 cm^{-1} indicating a large amount of *cis* isomer present. The mixture was dissolved in hexane, a few drops of iodine solution in petrol added and the solution left a day in daylight. The 938 cm^{-1} peak decreased and at the same time 1650 cm^{-1} peak came up and the 1630 cm^{-1} peak originally dominant, decreased.

Methyl-tetradeca-4,6,12-triene-8,10-diyn-oate-1. To 350 mg methyl-nona-4,6-dien-8-yn-oate-1, enriched in the all *trans* isomer as described above, was added 350 mg 1-bromopent-3-ene-yne-1, 2 mg cuprous chloride, 1 ml ethylamine (33 %), and 2 ml of tetrahydrofuran as solvent. The mixture was stirred until the reaction temperature had fallen to room temperature, then poured into petrol and a little ether. The solution was washed with water, dried and chromatographed on alumina. Pure ether eluted a pure diene-diyn-ene chromophore and methanol eluted an enediyn-ene chromophore. The ether eluates were distilled at 0.003 mm Hg (air bath 60–70°C), dissolved in chloroform and a trace of iodine added. The eluates were irradiated and finally re-distilled (UV-spectrum abs. max. at 3360, 3145, 2958, 2660, and 2490 Å).

The IR-spectrum had the following characteristics: Acetylenic bonds: 2200 and 2130 cm^{-1} of equal intensity, ester: 1740 and 1168 cm^{-1} , double bonds: 1640, 983, and 947 cm^{-1} .

Rather surprisingly methyl-tetradeca-4,6,12-triene-8,10-diyn-oate polymerises rapidly and has to be stored at –20°C in the presence of antioxidants.

Tetradeca-4,6,12-triene-8,10-diyn-ol-1. To 50 mg of the methyl-tetradeca-4,6,12-triene-8,10-diyn-oate-1, dissolved in 100 ml ether and cooled to –25°C (thermometer in the solution), was added a solution of 50 mg lithium aluminium hydride, also cooled to –25°C. The reaction was immediately stopped with water and the reduction product isolated in the usual way as a partly crystalline mass. The crude crystals were dissolved in petrol and chromatographed on alumina. Ether eluted an ene-diyn-en-ol chromophore produced in some side reaction: the first methanol eluates contained the desired diene-diyne-en chromophore. These fractions were isolated as usual and distilled at 0.001 mm Hg (air bath 65°C). The solid distillate was recrystallised from hexane until a melting point of 104–106°C was reached. No depression of melting point with XV obtained from saponification of the acetate B, was observed.

The UV-spectrum was identical in position and extinction with the above ester.

The IR-spectrum had the following characteristics: OH 3400, 1052, double bonds 1640, 982, 948, acetylenic bonds 2200 and 2130 cm^{-1} , the last one double the intensity of the first one.

S u b s t a n c e C

New fractions containing compounds with dienediyn-ene chromophores were eluted from the main column with ether and methanol just after the last chlorophyll coloured eluates. The substance C (m.p. 75–76°C) crystallised nicely from petroleum ether. The melting point remained constant on re-crystallisation.

The UV-spectrum was identical with those of A and B showing definite diene-diyn-ene chromophores.¹⁴ The IR-spectrum had the following characteristics: allylic hydroxyl 1088 and 1032, $\text{CH}_2=\text{CH}$ 3100, 1840, 910, *trans* diene 987, *trans* ene 948 and acetylenic bonds 2200 and 2125 cm^{-1} . This time the 2200 cm^{-1} peak had 160 % the intensity of the 2125 cm^{-1} peak, *i.e.* the usual intensity relation.

Catalytic hydrogenation. 39 mg C were hydrogenated with palladium in methanol and 30 ml hydrogen were consumed. The perhydro product solidified on distillation (crude m.p. 49.5–50.5°C, after re-crystallisation raised to 52–52.5°C). Analytical gas chromatography with the normal alcohols C_{15} – C_{18} as comparison substances proved the identity of the perhydro product and heptadecanol-1.

Manganese dioxide oxidation. 14.5 mg C in acetone solution was shaken with 76 mg active manganese dioxide¹¹ for 35 min and treated as usual. The diene-diyn-ene chromophore disappeared and a longer chromophore of less fine structure appeared. From petroleum ether 3 mg of the crystalline substance were obtained.

Absorption characteristics were as follows: UV-spectrum, 3680, 3450, 3190, 2860, 2670 Å, characteristic of diene-diyn-enal. IR-spectrum, CHO conj. 1683, 1120 cm^{-1} .

Synthesis of heptadeca-2,8,10,16-tetraene-4,6-diyn-ol-1. The triphenylphosphonium salt of 7-bromo-hept-ene-1 was prepared in the following way: 1.8 g 7-bromo-heptene-1 and 4 g triphenylphosphine were dissolved in 4 ml benzene and kept at 70°C for 2 days. A colourless syrup had separated out; the benzene solution was decanted off, and the syrup extracted thoroughly 3 times with ether. Finally 5 ml dry ether were added and the product placed in a beaker surrounded by dry ice and left for 2 days. The syrup solidified to a brittle mass, which could be crushed under ether and washed completely dry. The yield was 3.5 g, *i.e.* 75 % (m.p. 153–155°C; Bohlmann *et al.*¹⁸ report 167°C).

Dodeca-3,5,11-trien-1-yne. To 3 g of the phosphonium salt prepared as above was added 0.7 g pent-2-ene-4-yn-ol-1 dissolved in 50 ml dry benzene. The mixture was kept under pure nitrogen, stirred, and a solution of 0.165 g sodium in 5 ml absolute alcohol, diluted with 25 ml dry benzene, added slowly. The stirring was continued for 1/2 h. The reaction was stopped with water, and the benzene solution chromatographed on alumina. The hydrocarbon fraction was evaporated and distilled at 0.2 mm. (air bath 45–50°C).

The substance had the following absorption properties: UV-spectrum, 2610 Å with a shoulder at 2720 Å. IR-spectrum, monosubst. acetylene 3322 and 2100, vinyl 1828, 909 cm^{-1} .

The 10–11 μ region revealed a mixture of *cis* and *trans* compounds as was expected.

As a control, a small amount of the purified reaction product was hydrogenated; analytical gas chromatography revealed pure dodecane.

Heptadeca-2,8,10,16-tetraene-4,6-diyn-ol-1. 40 mg 1-bromopent-3-en-1-yn-ol-5 (m.p. 36°C) in 0.4 ml methanol was added to a mixture of 0.5 ml ethylamine (33 %), 1 mg cuprous chloride, 1 crystal hydroxylamine-hydrochloride and 40 mg dodeca-3,5,11-trien-1-yne in 0.5 ml methanol. The reaction temperature was 30°C. The reaction mixture was worked up at once and the crude coupling products isolated as usual. Unreacted components were evacuated off at 90°C (0.001 mm Hg). The coupling products which had moved into the upper part of the distillation bulb, were separated off. IR spectroscopy revealed that the coupling products contained some *cis* isomer as was expected from the synthesis of dodeca-3,5,11-trien-1-yne. *trans*-Isomerisation in light in the presence of iodine was unsuccessful. Chromatography on alumina impregnated with 10 % of a 5 % silver-nitrate solution led to a crystalline alcohol fraction (m.p. 73°C; no depression with pure C). Spectral data were also in agreement with those of C.

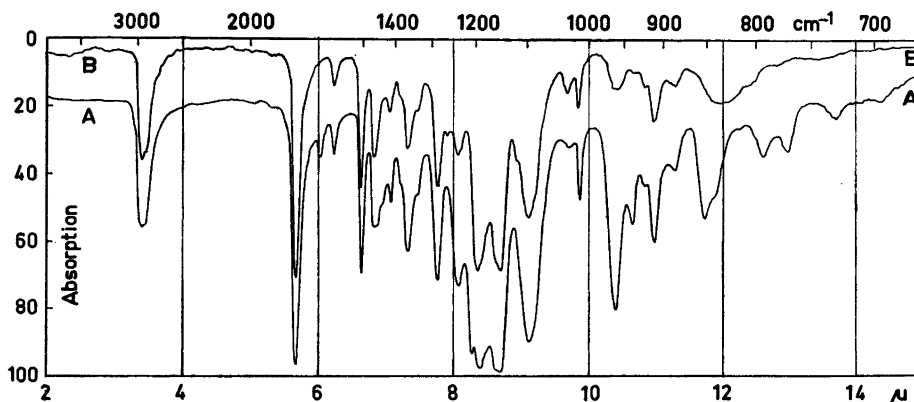


Fig. 2. Infrared spectra of A: Anol isovalerate; B: Dihydro-anol isovalerate.

Substance D

The 2530-chromophore which was eluted between A and B, could not be freed from A on repeated chromatography. Purification was achieved by preparative gas chromatography (195°C, column SE30). The fractions enriched in D were rechromatographed on alumina (Spencer) with petrol as eluant and obtained free of compounds with any longer chromophores. The liquid was re-distilled at 0.01 mm (air bath 60–65°C) and was pure when tested on the analytical column. The UV-spectrum exhibited a peak at 2530 Å ($E_{1\text{cm}}^{1\%} = 1120$) and inflections at 2970 and 2860 Å. The IR-spectrum is shown in Fig. 2.

Through the courtesy of Dr. J. Dale, elementary analysis was carried out at European Research Associates, Bruxelles, (Found: C 76.68; H 8.08; O 14.59. Calc. for $C_{14}H_{18}O_2$: C 77.03; H 8.31; O 14.66).

Catalytic hydrogenation of D. 32.7 mg D was hydrogenated in ethanol solution with palladium catalyst, the consumption stopped at about 1.5 mole hydrogen. The hydrogenation product was isolated as usual and distilled (UV-spectrum 2720, 2660 with definite shoulder 2800 Å, $E_{1\text{cm}}^{1\%} = 25$ viz. 32 on the double maximum).

The IR-spectrum is shown in Fig. 2.

Saponification of D. D was dissolved in alcoholic potassium hydroxide (about 1 N) and left for 1 h at room temperature. No chromophoric substance could be extracted with petroleum ether. Small amounts of a substance with absorption maximum at 2590 Å were extracted with ether. After acidification, this substance was extracted with petroleum ether and by evaporation immediately rendered a crystalline substance. After re-crystallisation it melted at 91–93°C. No melting point depression on admixture with authentic anol could be detected. The UV-spectrum in neutral and alkaline solution and the infrared spectrum confirmed the identity of the saponification product and anol.

Acknowledgement. We should like to express our warmest gratitude to Professor T. A. Geissman who made this investigation at all possible. Grants from *Norges Almenvitenskapelige Forskningsråd* to one of us (J.S.S.) are gratefully acknowledged.

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