

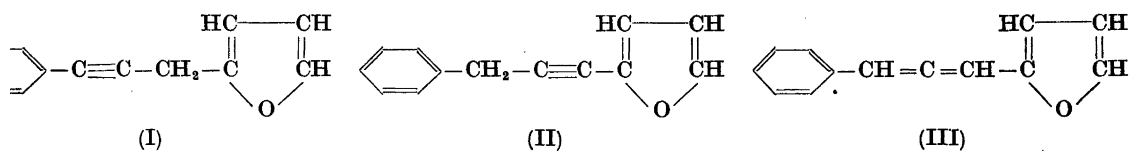
Studies Related to Naturally Occurring Acetylene Compounds. XIX. The Isolation of 1-Acetoxy-*n*-Trideca-2:10:12-triene-4:6:8-triyn-4-yl from *Carlina vulgaris* L.

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1-Acetoxy-*n*-trideca-2:10:12-triene-4:6:8-triyn-4-yl (V) has been isolated from common Carlinethistle, *Carlina vulgaris* L.* *eu-vulgaris* Holmboe. (V) is the main chromophore of the lipids of all parts of the thistle. (V) bears interesting relations to the "carlina oxide" (II) isolated from *C. acaulis* L. and to 1-phenyl-*n*-hept-5-ene-1:3-diyne-7-ol (VI) recently isolated as the acetate from some species of the genus *Coreopsis*.

More than 50 years ago F. W. Semmler¹ isolated the so-called "carlina oxide" from the essential oil of *Carlina acaulis* L. The degradational studies which Semmler himself carried out² left only three constitutional possibilities (I)-(III).



Of these three possibilities Semmler — lead by an irrational aversion against the occurrence of acetylenic compounds in nature — chose (III), and it remained for A. St. Pfau *et al.* in 1935³ to prove that "carlina oxide" has the constitution (II).

In this laboratory the essential oils from some two hundred plants belonging to the family *Compositae* have been investigated with regard to their content of acetylenic compounds. The old "carlina oxide" we have, however, so far never met with. It has to be added that none of the plants investigated by us were in a botanical sense close relatives to *C. acaulis* L. which belongs to the tribe *Cynareae*, subtribe *Carlininae*. A recent preliminary investigation of the

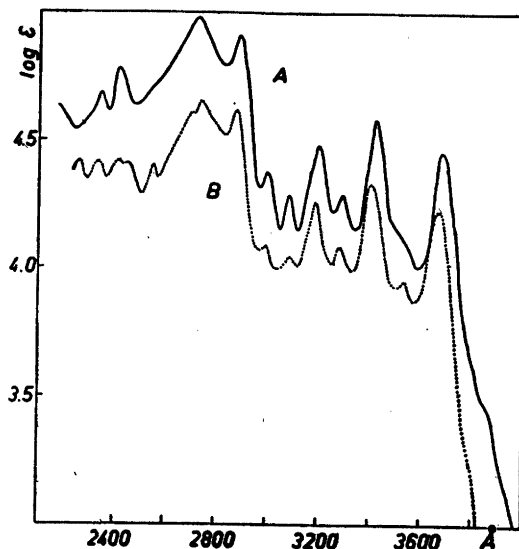
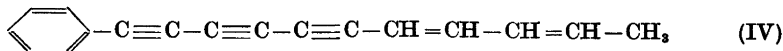


Fig. 1. Ultraviolet absorption in hexane of

- A: 1-acetoxy-*n*-trideca-2:10:12-triene-4:6:8-triyne (V) from *Carlina*.
 B: 1-phenyl-*n*-undeca-7:9-diene-1:3:5-triyne (IV) from *Coreopsis*.

essential oils from some members of the tribe *Cynareae*⁴ revealed that they contained some conjugated polyenyne, but we found no indication of the presence of "carlina oxide". *Carlina acaulis* L. does not occur in Norway, where the only members of the genus *Carlina* are two subspecies of *C. vulgaris* L., viz., *eu-vulgaris* Holmboe and *longifolia* (Rchb.) Neum. which occur in restricted areas of Southern Norway⁵. The starting material for our chemical investigations were seed samples of the subspecies *eu-vulgaris* Holmboe, most kindly collected by Dr. Hugo Sjörs in the surroundings of Uppsala in Sweden. The seed sample gave about 100 of this small prickly thistle. Qualitative investigations disclosed that acetone extraction at room temperature and steamed distilled essential oils gave the same U.V.-spectra, and that there were only slight differences between the spectra from the different parts of the thistle. All samples had strong selective absorption in the entire U.V.-region, with absorption maxima very close to that of 1-phenyl-*n*-undeca-7:9-diene-1:3:5-triyne (IV) isolated recently⁴ from some species of the genus *Coreopsis*.



By chromatographic analysis the essential oil from *Carlina vulgaris* was separated into a lot of fractions. Only the fractions containing the main chromophore have so far been worked up in detail. The main chromophore is retained on the alumina column until pure benzene or benzene-ethyl ether mixtures are used for elution. (IV) as a hydrocarbon is eluted already with

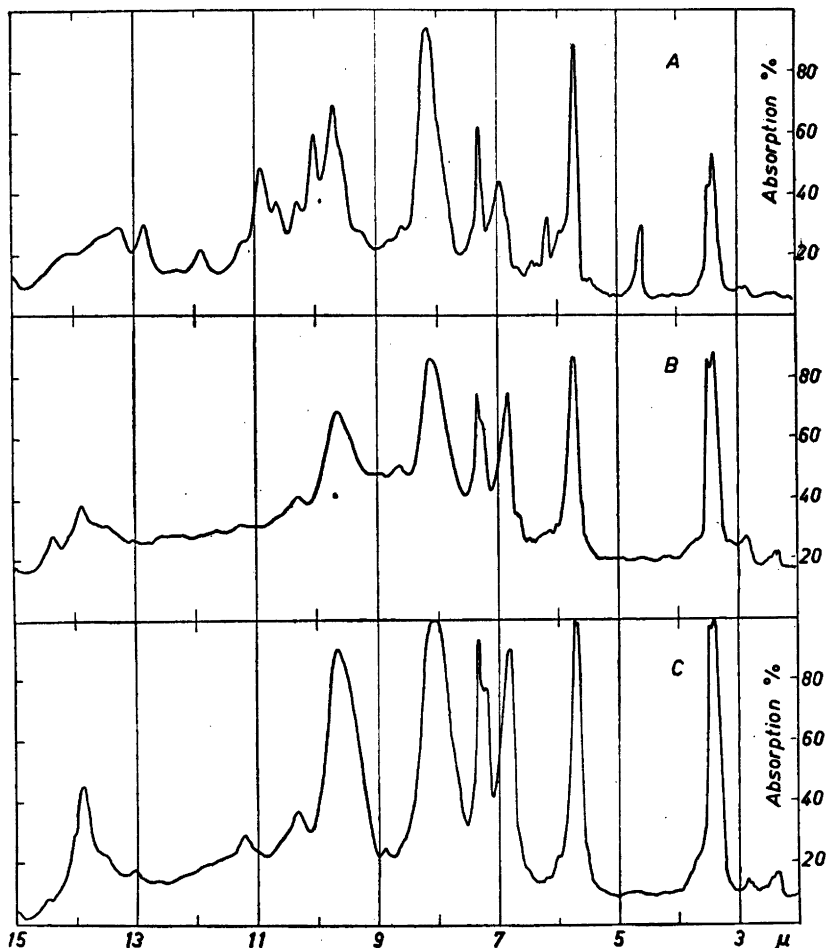


Fig. 2. Infrared absorption of

- A: 1-acetoxy-*n*-trideca-2:10:12-triene-4:6:8-triyne (V) liq., demontable cell, thickness ca. 0.01 mm.
 B: 1-acetoxy-*n*-tridecane from hydrogenation of (V), liq., thickness ca. 0.01 mm.
 C: 1-acetoxy-*n*-tridecane synthetic, liq., thickness ca. 0.025 mm.

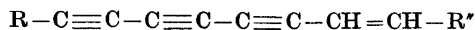
2—5 % benzene in petroleum ether and so it was obvious that the *Carlina* chromophore contained some more polar groups. By a combination of partial distillation and rechromatography the main chromophore was purified to constant spectral properties. The pure compound was a slightly yellow liquid, which solidified at -15° . We have found no solvent suited for recrystallisation. Our best fractions melted somewhat above -15° . The U.V.-spectrum in hexane is given in Fig. 1 together with that of (IV). The conformity is rather striking. The infra-red spectrum, Fig. 2, curve A, besides confirming the

acetylenic nature of the substance revealed two important facts, firstly that the *Carlina* chromophore was an acetate, sharp peak at 1750 cm^{-1} strong band at 1225 cm^{-1} ; secondly there was no indication of a phenyl residue as in (IV).

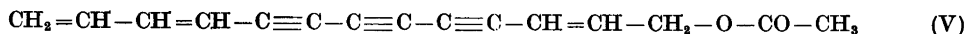
The perhydro compound, prepared by catalytical hydrogenation, had an infra-red spectrum, Fig. 2, curve B, which resembled very much that of *n*-decylacetate which we had obtained by hydrogenation of the matricarianyl acetate from some *Aster* and *Grindelia* species⁶. Thus obviously the hydrogenated compound is an aliphatic acetate.

This perhydro ester was saponified. The unsaponifiable part turned out to be *n*-tridecan-1-ol as shown by mixed m.p. with authentic material.

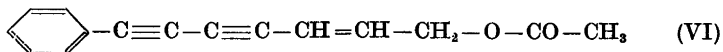
The *Carlina* chromophore reacted slowly with maleic anhydride. Although the amount of adduct obtained was too small for analysis, its U.V.-spectrum furnished valuable information. The sharp U.V.-maxima of the adduct agreed with that of a ketone isolated from *Artemisia vulgaris*⁷, which has an isolated carbonyl function and a conjugated ene-triene system of the type



In the *Carlina* chromophore the diene system which have reacted with maleic anhydride must take part in the end residue R to account for the striking conformity of the U.V. spectrum of (IV) with the *Carlina* chromophore. Therefore the acetate group must be present in R'. Since the infra-red spectrum informs us that the acetate ester group is not a vinyl ester, R" must be $-\text{CH}_2-\text{O}-\text{CO}-\text{CH}_3$. The *Carlina* chromophore then is given the structure (V) of 1-acetoxy-*n*-trideca-2 : 10 : 12-triene-4 : 6 : 8-triene.



Professor E. R. H. Jones and Dr. M. C. Whiting have, as mentioned in the XVIIth-communication⁴ of this series, pointed out the analogy between the prototropic rearrangement of pentenynol to α -methyl furan⁸ and an isomerisation of 1-phenylhepta-5-ene-1 : 3-diyne-7-ol, found as the acetate (VI) in some *Coreopsis* species, to the "carlina oxide" of *C. acaulis*



The alcohol corresponding to (V), the main chromophore of the essential oil of *C. vulgaris*, the alcohol corresponding to (VI) and the "carlina oxide" all have the formula $\text{C}_{13}\text{H}_{10}\text{O}$. That the furan ring in (II) has arisen through some rearrangement similar to the prototropic rearrangement of acetylenic compounds to furan-derivatives as demonstrated by I. M. Heilbron *et al.*⁸ is very likely; the constitution (V) ascribed to the *C. vulgaris* chromophore raises the interesting question whether the phenyl residue in (II) and (VI) is formed by curling up of the dienyne tail of (V).

EXPERIMENTAL

The starting material consisted in part of acetone extracts obtained at room temperature and of steam distilled oils of the roots, the stem + leaves, and of the flower heads of the small thistle. All crude oils were chromatographed in petroleum ether solution on slightly deactivated alumina followed by elution with benzene-petroleum ether mixtures of per centage 10, 25, 50 and 100 benzene, ethyl ether and methanol.

Only the fractions eluted with 50 % benzene contained substances with long-wave selective absorption in the U.V. The first of these fractions showed absorption bands at 3 320, 3 140 and 2 580 ÅU. This chromophore accompanied also the main chromophore in the benzene and benzene-ether eluates. By the distillation of these fractions at 0.0001 mm the substance with a first max. at 3 320 distilled somewhat earlier, air bath temperature < 70°, than the main chromophore, which may be distilled at this pressure with air bath temperature at about 80°.

The distillates were rechromatographed on deactivated alumina, and then crystallised at -15°. U.V.-spectrum, Fig. 1.

ϵ_{\max}	28 900	39 000	19 500	30 600	19 500	24 000	81 400	95 600	66 400	49 000	
λ_{\max}	3 685	3 420	3 300	3 195	3 085	3 000	2 890	2 725	2 415	2 345	ÅU
$\Delta\nu_{\max}10^{-12}$	63.1	61.7	61.1								
	63.3										

Infra-red spectrum, Fig. 2 curve A.

Catalytical hydrogenation: 10.5 mg substance was hydrogenated in alcoholic solution with a Pd/BaSO₄-catalyst. Consumed, $t = 21^\circ$, $p = 755$ mm, 10.9 ml H₂; calculated for C₁₅H₁₂O₂, 3/≡, 3/= 10.5 ml. The hydrogenation product was isolated in the usual way and distilled at the oil pump. Infra-red spectrum Fig. 2 curve B, synthetic 1-acetoxy-*n*-tridecane Fig. 2 curve C.

The hydrogenation product was saponified with alcoholic potassium hydroxide and the unsaponifiable part isolated. After distillation at 3 mm/air bath temperature 100° the product melted at 17.5–18.5°, crystallised from hexane m. p. 24°, recrystallised, m. p. 26.5–26.7°.

For comparison *n*-tridecan-1-ol was synthesised by the Grignard reaction of lauryl bromide with trioxymethylene according to Ou⁹. Synthetic *n*-tridecan-1-ol m. p. 28°, literature¹⁰ 30.5°. Mixed m. p. of the unsaponifiable matter from the hydrogenation of the *Carlina* chromophore with synthetic *n*-tridecan-1-ol 27.5–28°. For comparison a mixed m. p. determination was carried out on a mixture about 1:3 of synthetic *n*-dodecanol and *n*-tridecanol, found unsharp melting range 23–26°.

Maleic anhydride adduct. 3 mg of pure *Carlina* chromophore was dissolved in pure benzene and a large excess of freshly sublimed maleic anhydride dissolved in benzene was added, and the solution left at room temperature under nitrogen for 2 hours. A sample showed that the U.V.-spectrum had not changed. The solution was then sealed up in a glass tube under pure nitrogen and heated at 75° for 1 ½ hours. A U.V.-spectrogram revealed that still no reaction had taken place.

A solution of about 2 mg of pure *Carlina* chromophore in benzene was illuminated for 1 ½ hours with a mercury lamp. Again the U.V.-spectrum of a sample revealed that the chromophore had not changed. To the irradiated solution a saturated solution of maleic anhydride in benzene was added the solution sealed up under pure nitrogen and heated at 60° for 3 hours. The solvent and the excess of maleic anhydride were removed at 40° and 0.0001 mm. The residue was rather insoluble in petroleum ether; it was dissolved in a little ethyl ether and diluted with spectral hexane. U.V.-maxima

maleic anhydride adduct:	3 320	3 108	2 905	2 740	—	2 450	ÅU
R—C≡C—C≡C—C≡C—CH=CH—R'':	3 286	3 086	2 890	2 725	2 577	2 425	*

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