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Studies Related to Naturally Occurring Acetylene Compounds. XV. The Isolation of *trans*-Lachnophyllum Ester from *Bellis perennis* L

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In the preceding communication of this series [1] we demonstrated that acetylenic compounds are widely distributed in the tribus *Astereae* of the plant family *Compositae* and that to some extent some of the investigated genera are chemically characterised by the occurrence of specific acetylenic compounds in certain parts of the plants. With the object to collect experimental data, which perhaps once in the future might render contributions to the genesis of these genera, we have tried to investigate as many species as possible within the tribus *Astereae*. One of the few genera of *Astereae* which are represented in Scandinavia is *Bellis* as the well known daisy, *Bellis perennis* L. Wild the daisy occurs only in the coastal district of western Norway. It has, however, spread into lawns in many cultivated places. It is very scarce in the Trondheim district, but from a small collection we prepared a small sample of the essential oil of daisy, which gave a preliminary indication as to the nature of the chromophoric system. The oil from the overground parts was devoid of acetylenic chromophores. In the U.V.-spectrum of the root oil definite maxima occurred at:

λmax., oil from the root of daisy:	3 350	3 045	2 865	2 705	2 565	2 227
» *trans*-lachnophyllum ester [4]:		3 053	2 872	2 710	2 568	2 235
» *cis*- » » [5]		3 094	2 913	2 760	—	2 245

The 3 350 maximum agrees with the first maximum of the matricaria ester (II) [2,3], the following 5, as is seen from the collocation of data above, with those of *trans*-lachnophyllum ester.

trans-Lachnophyllum ester (I) is so far known only from

$$CH_3—CH_2—CH_2—C\equiv C—C\equiv C—CH=CH—COOCH_3 \quad (I)$$

$$CH_3—CH=CH—C\equiv C—C\equiv C—CH=CH—COOCH_3 \quad (II)$$

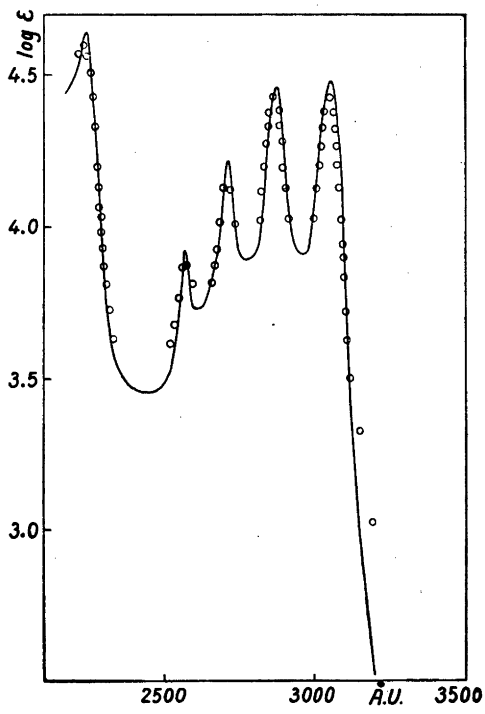

Fig. 1. Ultraviolet absorption in hexane of trans-lachnophyllum ester $CH_3-(CH_2)_2-C\equiv C-C\equiv C-CH=CH-COOCH_3$
——— *synthetic*
⊙⊙⊙⊙ *from root of Bellis perennis L.*

the synthesis, reported in the third communication of this series. The *cis*-isomer, which was discovered in *Lachnophyllum gossypinum* Bg. already in 1935 by Wiljams *et al.*[6], has been shown to be present in several essential oils from plants belonging to the *Compositae* [5,7]. We thus found it desirable to establish if the absorption maxima of the oil of the daisy root really belonged to the *trans*-isomer (I) or to quite another compound. As no further quantities of the wild daisy were available in Trondheim, we, of course, tried the much larger cultivated variants. To our disappointment it turned out that the essential oil from different cultivated varieties contained a mixture of compounds, which, to judge from the U.V.-spectra, contained about equal amounts of matricaria and lachnophyllum esters. As usual our attempts to separate this mixture by chromatography was completely unsuccessful. Thanks to energetic assistance by Miss Sonja Lystad some kilograms of the tiny root of the wild daisy were dug out from the abundant occurrences round Stavanger, in fact the procurement of the starting material was the most difficult part, and we are greatly indebted for this valuable aid. The separation of the *trans*-lachnophyllum ester from the minor amounts of matricaria ester and other compounds present was tedious, but led, as described in the experimental part, to a final fraction with the correct U.V.-spectrum of *trans*-lachnophyllum ester (*cf.* Fig. 1). The m.p. of this fraction was 16—17°, whereas 19° was given by Bruun *et al.* Of the original preparation only some mg were left, which yet showed the m.p. 15.5—16°. The amount did not allow a repurification. The

mixed m.p. was undepressed. Thus there should be no doubt that the main U.V.-maxima of the oil of the daisy root originate from the presence of the *trans*-isomer of (I).

We have not succeeded in the crystallisation of the matricaria ester from any of the chromatographic fractions enriched in that chromophore. Since 2-*cis*:8-*cis*-matricaria ester has an outstanding crystallising power, we doubt that this isomer may be present. It would be rather surprising, too, if an essential oil, which contains the *trans*-isomer of (I), should also contain the *cis* : *cis*-isomer of (II). It would be interesting to know what stereoisomer of (II) is present in daisy oils. From the unusual occurrence of *trans*-I one would expect that 2-*trans* : 8-*trans*-(II), might be found to be a naturally occurring substance. It is to be hoped that some of the other species of *Bellis* have more favourable mixtures of these acetylenic esters.

EXPERIMENTAL

The starting material consisted of the roots of some thousand plants of the wild daisy collected at Hillevåg near Stavanger and the roots of further one thousand cultivated daisies belonging to different giantvariants. When small scale extraction experiments had revealed that the yield of acetylenic compounds was the same as with steam distillation, all root material was steam distilled, total yield of essential oil 1 300 mg. In portions of about 150 mg this oil was chromatographed from petroleum ether solution on neutral alumina. The material was eluted with mixtures of petroleum ether and benzene with 10, 25, 50, 75 and 100 % of benzene. The lachnophyllum ester chromophore concentrated in the first fractions of 50 % benzene. The fractions, which according to their U.V.-spectra contained the purest chromophore, were combined and rechromatographed, with elution this time with 40 and 60 % benzene in petroleum ether. The purest fractions were combined and rechromatographed. The first washings with 40 % benzene then eluted an oil, which was practically devoid of the 3 350 chromophore in the U.V.-spectrum. This fraction (178 mg) was distilled slowly at 2×10^{-4} mm and the fraction 45—52° (airbath) was collected. This fraction solidified in the cold and could be crystallised from petroleum ether solution when cooled to −30°, m.p. 12.5—14°. These crystals (2.8 mg) were recrystallised from dilute alcohol, white needles m.p. 16.0—17.0°, mixed m.p. with synthetic (I) 16°. U.V.-spectrum *cf.* Fig. 1.

The chromatographic fractions from which the isolation of *trans*-lachnophyllum ester was successful, amounted to only some 14 % of the *Bellis* oil. In the fractions with pure benzene a chromophore was enriched with maxima close to those of lachnophyllol. The extinction coefficients were low and distillation at 0.001 mm separated these chromatographic fractions into different substances. The purest chromophore was found in the fraction b.p. 73—100°/0.0001 mm.

U.V.-maxima of this fraction:	λ max	2 830	2 678	2 527	ÅU	
	$E^{1\%}_{1\,cm}$	155	191	141		
$CH_3-(CH_2)_2-C\equiv C-C\equiv C-CH=CH-CH_2OH$ (= lachnophyllol)						
	λ max	2 825	2 665	2 520	2 395	ÅU
	$E^{1\%}_{1\,cm}$	1 320	1 480	990		

This fraction was saponified at 0° with sodium hydroxyde in acetone-water solution under pure nitrogen. Neither the unsaponifiable, nor the acid product showed selective absorption, both exhibiting only an undistinct step out below 3 100 Å. When the acid fraction had remained for some weeks in spectral hexane solution at −17°, white crystal clusters had separated, weight 1.4 mg, m.p. rather distinct at 115—117°. In order to dissolve these crystals in the original amount of spectral hexane, they had to be dissolved

in a few drops of alcohol, and this solution rapidly diluted with spectral hexane. To our surprise these crystals gave a spectrum very close to that of the lachnophyllum ester (3 045, 2 863, 2 710, 2 565). Recrystallisation brought the m.p. to 120—122.5°. As the amounts were insufficient for analysis, the *cis*- and *trans*-lachnophyllum acids were prepared for comparison by saponification of the corresponding methyl esters. *cis*-Lachnophyllum acid m.p. 72—73° undistinct, *trans*-lachnophyllum acid m.p. 123.5—124.5°. The mixed m.p. between the crystals from the essential oils of *Bellis* and the *trans*-acid was undepressed: 120.5—124.5°. By this saponification *trans*-lachnophyllum acid has obviously arisen through some displacement of an ene-diyne-chromophore into conjugation with a carboxyl group.

Similar changes in chromophores by saponification has been observed by Kavanagh *et al.*[8] with nemotin, by Anchel [9] with Drosophilin D, both acetylenic antibiotics from *Bassidiomycetes*.

The amounts available of oil of daisy prevent the elucidation of the structure of the compound which rearranges into *trans*-lachnophyllum acid. The observed rearrangement might indicate that the unusual occurrence of the *trans*-isomer of lachnophyllum ester in oil of daisy originates in a secondary displacement of the chromophoric system. The acidbase catalysed displacement of conjugated systems are known to lead to *trans*-isomers.

SUMMARY

From the essential oil of daisy there has been isolated the *trans*-isomer of lachnophyllum ester (I) whereas all hitherto known occurrences of this ester in nature comprise the *cis*-isomer. A chromatographic fraction of the daisy oil, which originally showed an ene-diyne chromophore, rearranged on saponification into an acid which turned out to be *trans*-lachnophyllum acid.

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