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POLYACETYLENIC C_{14}-EPOXIDE AND C_{14}-TETRAHYDROPYRANYL COMPOUNDS FROM *DAHLIA SCAPIGERA**

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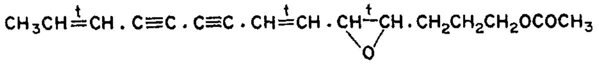
Abstract—A new polyacetylenic epoxide (1-acetoxy-4,5-epoxy-tetradeca-6,12-diene-8,10-diyne) has been isolated together with tetrahydro-2-(non-1,7-diene-3,5-diynyl)pyran-3-ol from *Dahlia scapigera* (A. Dieter) Link et Otto var. *scapigera* forma *merckii*. The two compounds are assumed to be biogenetically related. The content of polyacetylenes in the species is summarized.

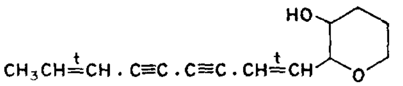
INTRODUCTION

IN A PAPER[1] on polyacetylenes in the genus *Dahlia* we reported the presence of a polyacetylene epoxide in *Dahlia scapigera* (A. Dieter) Lind et Otto var. *scapigera* forma *merckii*. The epoxide was characterized as 1-acetoxy-4,5-epoxy-tetradeca-6,12-diene-8,10-diyne (I).



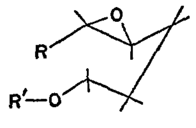
$$CH_3CH\overset{t}{=}CH\cdot C\equiv C\cdot C\equiv C\cdot CH\overset{t}{=}CH\cdot \underset{\diagdown O\diagup}{CH\overset{t}{-}CH}\cdot CH_2CH_2CH_2OCOCH_3$$

I

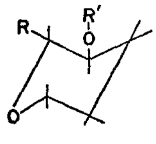


II .

Further work on the same species has now revealed the presence of the tetrahydropyranyl-acetylene II. This fact is very interesting from a biogenetic point of view as an epoxide, such as III, may be the precursor of the tetrahydropyranyl compound IV as already postulated by Jones[2] and Bohlmann.[3]



III



IV

$R = CH_3CH{=}CH\,(C{\equiv}C)_2\,CH{=}CH-$

$R' = \begin{cases} H \\ \text{or} \\ Ac \end{cases}$

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* Part VI in the series "Chemical Constituents of the Genus *Dahlia*".

[1] J. LAM and F. KAUFMANN, *4th International Symposium in the Chemistry of Natural Products*, Stockholm June 26th to July 2nd (1966).

[2] E. R. H. JONES, *Chem. Brit.* **6**, (1966).

[3] F. BOHLMANN, *Fortschr. Chem. Org. Naturst.* XXV, 25, 37 (1967).

The tetrahydropyranyl compound is known from other *Dahlia* species, whereas the epoxide has not been isolated before.

DISCUSSION AND RESULTS

The identity of the tetrahydropyranyl compound (λ_{max} = 313, 294, 277, 262, 249, 239 and 231 nm) was proved mainly on basis of the mass spectrum (Fig. 1) identical with the spectrum of tetrahydro-2-(non-1,7-diene-3,5-diynyl)pyran-3-ol published by Safe,[4] but the IR and the NMR spectra were also in agreement with the structure.

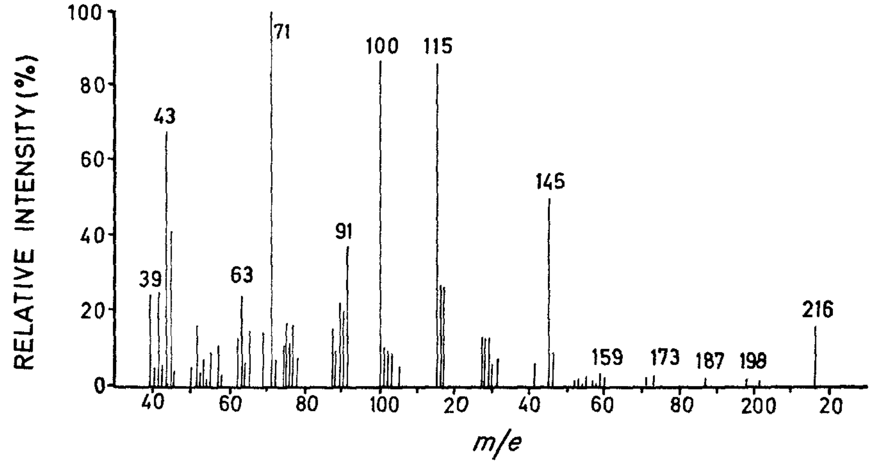

FIG. 1.

The epoxide was isolated in very small amounts from the fresh tubers and despite attempt to purify the compound by repeated column and TLC, it was not possible to obtain a crystalline product. The grade of polarity of the compound indicated an ester. The UV spectrum (λ_{max} = 317, 298, 281, 266, 252·5 and 243 nm) indicated a compound with an elongated ene-diyne-ene chromophore. Hydrolysis with sulphuric acid gave a compound with a pure ene-diyne-ene chromophore (λ_{max} = 313, 294·5, 277·5, 261·5, 249 and 240 nm). The hydrolysis product (a 1,4,5-triol) was isolated from the reaction mixture by ether extraction and oxidized with periodic acid giving a compound which, according to the UV spectrum and TLC behaviour, was identical with matricarinal (2,8-diene-4,6-diyne-deca-1-al). It has not been possible to isolate the other oxidation product (4-hydroxy-butyraldehyde) as such or as a derivative which according to the structural formula for the epoxide should also be formed. The IR and NMR spectra (see Experimental) of the epoxide are in agreement with the proposed structure, and furthermore indicate that the configuration is is all-*trans*.

Besides these two compounds from this dahlia we have isolated several others some of which we have reported earlier.[5] The situation is summarized in Tables 1 and 2.

The amounts of VI and VII were much higher in the previous investigation (1965). The difference may be due to a seasonal variation which is obviously also to be found within the

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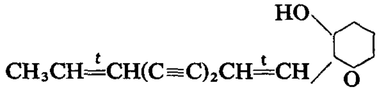
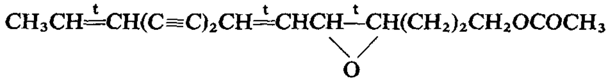
[4] S. H. SAFE, Ph.D. Thesis, The Dyson Perins Laboratory, University of Oxford (1965).

[5] F. KAUFMANN and J. LAM, *Acta Chem. Scand.* **19**, 1267 (1965).

TABLE 1. CONSTITUENTS ISOLATED FROM THE TUBERS AND ROOTS*

		Date	
		1/10/69	7/11/69
I	$CH_3CH\overset{t}{=}CH\,(C\equiv C)_4CH\overset{t}{=}CH_2$	2	8
II	$CH_3CH\overset{t}{=}CH(C\equiv C)_3CH\overset{t}{=}CHCH{=}CH_2$	§	§
III	$CH_3CH{=}CH(C\equiv C)_2(CH\overset{tt}{=}CH)_2CH{=}CH_2$	8	2
IV	$CH_3(CH\overset{tt}{=}CH)_2C\equiv C(CH\overset{tt}{=}CH)_2(CH_2)_4CH_2OCOCH_3$	32	14
V	$CH_3(CH\overset{tt}{=}CH)_2C\equiv C(CH\overset{tt}{=}CH)_2(CH_2)_4CH_2OH$	4	9
VI	$CH_3CH\overset{t}{=}CH(C\equiv C)_2(CH\overset{tt}{=}CH)_2(CH_2)CH_2OCOCH_3$	570	310
VII	$CH_3CH\overset{t}{=}CH(C\equiv C)_2(CH\overset{tt}{=}CH)_2(CH_2)_2CH_2OH$	132	275
VIII		—	31
IX	 $CH_3CH\overset{t}{=}CH(C\equiv C)_2CH\overset{t}{=}CHCH\overset{t}{-}CH(CH_2)_2CH_2OCOCH_3$	—	§

* Mg/kg fr. wt. determined by UV spectroscopy.
§ Amounts less than 0·02 mg/kg fr. wt.

TABLE 2. CONSTITUENTS ISOLATED FROM THE AERIAL PARTS

IV	$CH_3(CH\overset{tt}{=}CH)_2C\equiv C(CH\overset{tt}{=}CH)_2(CH_2)_5OCOCH_3$
V	$CH_3(CH\overset{tt}{=}CH)_2C\equiv C(CH\overset{tt}{=}CH)_2(CH_2)_5OH$
X	$CH_3(CH\overset{tt}{=}CH)_2C\equiv C\cdot CH_2CH\overset{c}{=}CH(CH_2)_6OCOCH_3$
XI	$CH_3CH\overset{t}{=}CH(C\equiv C)_2CH_2CH\overset{c}{=}CH(CH_2)_6OCOCH_3$
XII	$CH_3CH\overset{t}{=}CH(C\equiv C)_2CH_2CH\overset{c}{\ }CH(CH_2)_6OH$

same year 1969, when the acetylenes are isolated from material with about one month between harvesting. In 1964 the material was harvested in July.

No attempts were made to quantify the amounts of the polyacetylenes present in the aerial parts of the plant, as they are all substances known from the related *Dahlia merckii* Lehm. reported by Bohlmann.[6]

It may be noted that cosmene is present in the flowerheads as well as in the leaves in large amounts (0·35% and 0·19% of the fresh material, respectively). Cosmene is widely distributed in Coreopsedinae (Heliantheae).

EXPERIMENTAL

The extraction of the plant material, chromatography of the extracts, and isolation of the individual compounds were carried out immediately after harvesting of the plants following the same procedure as described previously.[7]

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[6] F. BOHLMANN and K.-M. KLEINE, *Chem. Ber.* **98**, 872 (1965).

[7] J. LAM, F. KAUFMANN and O. BENDIXEN, *Phytochem.* **7**, 269 (1968).

1-*Acetoxy*-4,5-*epoxy*-*tetradeca*-8,10-*diyne*-6,12-*diene*

The epoxide was isolated in a yield of 0·0006% based on the weight of the fresh plant material. The compound was a faint yellow oil obtained after repeated column-chromatography and a final purification by TLC. The compound gave only one spot by TLC when eluted with various solvents. λ_{max} (EtOH) 318 (ϵ = 20,500), 298 (25,100), 281 (19,450), 266 (11,900), 252·5 (24,800), and 243 (33,100) nm; ν_{max} (film) 2950, 2220 (—C≡C—), 2140 (—C≡C—), 1740 (>C=O), 1630 (—C=C—), 1440, 1360, 1040 ($\underset{\overset{\diagdown\diagup}{\mathrm{O}}}{>\mathrm{C{-}C}<}$), 1240 (OAc), 945 (*trans*—CH=CH—), 880 (*trans*—$\underset{\overset{\diagdown\diagup}{\mathrm{O}}}{\mathrm{HC{-}CH}}$—) cm^{-1}. τ ($CDCl_3$) 7·9 (s, CH_3—C=O), 8·1 (dd, J = 7 and 1·5 Hz, $\mathrm{CH_3{-}\overset{|}{C}{=}\overset{|}{C}{-}}$), 8·2–8·3 (m, —$(CH_2)_2$—), 5·8 (t, J=6 Hz, —CH_2—O—C=O), 6·8 (m, $=\mathrm{C{-}}\underset{\overset{\diagdown\diagup}{\mathrm{O}}}{\mathrm{CH{-}C}<}$), 7·1 (m, $=\overset{|}{\mathrm{C}}\overset{\diagdown}{-}\mathrm{C{-}}\underset{\overset{\diagdown\diagup}{\mathrm{O}}}{\mathrm{CH{-}C}<}$), 3·5–4·7 (m, olefinic protons).

Hydrolysis

1 mg of the epoxide (in 1 ml Et_2O) was mixed with 5 ml of dioxane and 3 ml of N H_2SO_4. The mixture was kept at 80–85° for 2 5 hr, diluted with H_2O, and extracted with Et_2O giving a compound (1,4,5-trihydroxy-tetradeca-8,10-diyne-6,12-diene) with λ_{max} = 312, 293·5, 276·5, 261, 254, 248·5 and 239 nm.

Oxidation

10 mg of the epoxide was hydrolysed as described above and the Et_2O extract was concentrated to 2 ml. This solution was agitated vigourously with a solution of 30 mg HIO_4 in 5 ml H_2O for 2 5 hr. The Et_2O phase contained matricarianal, λ_{max} (Et_2O) 338 5, 317 5, 297, 283, 261 and 250 nm.

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