

same, apart from the difference between $\text{CO} \cdot \text{NH} \cdot \text{CO}$ in glutarimide and $\text{O} \cdot \text{CH} \cdot \text{CH}_2\text{OH}$ in ribose. It is evident that the thalidomide molecule is similar in size and shape to those of the nucleosides. There is also resemblance in the general distribution of polar groups. On the other hand, the compounds differ widely in chemical behaviour and ability to form hydrogen bonds.

It would appear worth while to consider the possibility that the biological effects of thalidomide may in part be related to its structural resemblance with nucleosides. Perhaps thalidomide is an antagonist to one or more nucleosides and/or nucleotides. It could, because of its similar shape, size and van der Waals field of force, partially block an enzyme, causing interference with nucleic acid and protein synthesis, or with other metabolic processes involving nucleosidic structures. Less likely, it may also be conceived that thalidomide interacts directly with nucleic acid structure, either temporarily, or by intercalation of its phthalimide part between bases in a manner resembling that proposed for proflavine.⁷ This would be due to attraction between the planar parts of the molecules. The similarity in the disposition of the hydrogen atoms at C(2') and C(3') may also play a role.

A number of investigations of the influence of thalidomide on embryonic development has been carried out and several theories proposed,⁸⁻¹⁰ but its mode of action still appears to be unknown.

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Chemical Constituents of the Genus *Dahlia*

Two Polyacetylenic Compounds from *Dahlia scapigera* Link et Otto

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A recent communication by Bohlmann and Kleine¹ on acetylenes from *Dahlia merckii* Lehm. prompts us to report on two acetylenes which we have isolated independently.

By chromatography of a light petroleum extract of the roots and tubers of *Dahlia scapigera* (A. Dietr.) Link et Otto var. *scapigera forma merckii* (Lehm.) Sherff, two colourless acetylenic compounds A and B were eluted. Both are present in large amounts (A: 0.1%, B: 0.1% based on the weight of fresh material).

Compound A is eluted easily with light petroleum and melts at 29.5–31.0°. In the ultraviolet region it has the following peaks: 250, 266.5, 280, 296.5, 315, and 336 m μ (ϵ : 29 400, 25 800, 15 100, 26 100, 35 300, and 26 100). (The molecular extinctions are calculated on basis of molecular weights corresponding to C₁₃-compounds).

Compound B is more polar and can be eluted with a mixture of light petroleum and ether. After purification by preparative thin-layer chromatography the compound melts at 111.0–111.5° and exhibits an ultraviolet spectrum nearly identical with that of compound A: 250, 266.5, 280, 296.5, 315, and 336 m μ (ϵ : 31 500, 27 950, 16 500, 28 700, 39 100, and 28 800).

The infrared spectrum of A is indicative of an acetoxygroup (1750 cm⁻¹, 1240 cm⁻¹) and that of B of a primary alcohol group (3630 cm⁻¹, 1050 cm⁻¹, 1290 cm⁻¹). Further bands observed for A are: $-\text{C}\equiv\text{C}-$ (2210 cm⁻¹, 2140 cm⁻¹), *trans* $-\text{CH}=\text{CH}-$ (945 cm⁻¹) and *trans-trans* $-(\text{CH}=\text{CH})_2-$ (1640 cm⁻¹, 980 cm⁻¹). The spectrum of compound B shows $-\text{C}\equiv\text{C}-$ (2200 cm⁻¹, 2130 cm⁻¹), *trans* $-\text{CH}=\text{CH}-$ (949 cm⁻¹), and *trans-trans* $-(\text{CH}=\text{CH})_2-$ (1635 cm⁻¹, 985 cm⁻¹) absorptions.

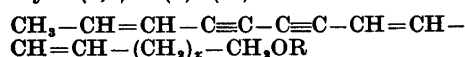
Hydrolysis of A (purified by preparative thin-layer chromatography) with methanolic potassium hydroxide afforded a compound with m.p. 110.5–111.5° and

unchanged ultraviolet spectrum. The hydrolysis product was chromatographically identical (TLC) with an authentic sample of B.

B gives a Diels-Alder adduct with maleic anhydride, m.p. 153–154°, and ultraviolet maxima at 216.5, (288), 240.5, 253.5, 267.5, and 284 μ (ϵ : 24 100, 5130, 6870, 12 200, 16 670, and 12 000).

The microanalytical data suggest that A and B are C_{13} - or possibly, C_{14} -compounds. (Found for A: C 78.61, 78.59; H 7.36, 7.40. Calc. for $C_{13}H_{16}O_2$: C 78.94; H 7.02 and for $C_{14}H_{18}O_2$: C 79.32; H 7.47. Found for B: C 83.37, 83.37; H 7.87, 7.92. Calc. for $C_{13}H_{14}O$: C 83.8; H 7.52 and for $C_{14}H_{16}O$: C 83.92; H 8.03).

Compounds possessing the terminal grouping $CH_3-CH=CH-C\equiv C-$ are characteristic for the polyacetylenes of the subtribe *Heliantheae*, to which *Dahlia* belongs. Therefore, at this stage of our investigation, we supposed A to be the acetate (I) of B, trideca-triene-(3,5,11)-diyne-(7,9)-ol-(1) (II).

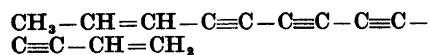


I: R = CH_3CO- , $x = 1$;

II: R = H, $x = 1$;

Ia: R = CH_3CO- , $x = 2$

Iia: R = H, $x = 2$



III

The NMR-spectrum* of A (in CCl_4) displays a triplet at 6.00 τ ($J = 6.5$ cps) which is typical for the $-CH_2-OAc$ group. Furthermore, an olefinic multiplet in the region 3.2–4.6 τ and a multiplet in the region 7.96–8.90 τ can be assigned to the methylene and methyl protons. The terminal methyl group gives a double doublet at 8.15 τ ($J = 6.5$ cps and 1.2 cps). A double quartet, from $Me-CH=C-C\equiv C-$, appears at 3.60 τ ($J = 15.5$ cps and 6.5 cps). The signals from

* The NMR-data were obtained by the courtesy of Dr. K. Schaumburg, H. C. Ørsted Institute, Copenhagen.

$Me-C=CH-C\equiv C$ are found as another double quartet at 4.46 τ ($J = 15.5$ cps and 1.2 cps). The integrated signals over the three regions give the proton distribution 2:6:10. This is not in agreement with the proposed C_{13} -compounds but rather indicates that A and B represent the analogous C_{14} -compounds (Ia and Iia). This conclusion is the same as that arrived at by Bohlmann and Kleine.¹

Among the *Dahlia* species under examination, *Dahlia* cfr. *pinnata* Cav. and *Dahlia coccinea* Cav. var. *coccinea*, contain substances exhibiting UV.-spectra indicating the same chromophoric system as that present in the above mentioned alcohol and the corresponding acetate, but thin-layer chromatography revealed differences between the R_F -values, indicating that the compounds of these *Dahlia* species are not identical with those described in the present communication.

In roots and tubers from all three plants we have shown the presence of the well-known tetrayne (III). A woody species, *Dahlia lehmannii* Hieron., apparently differs from the other species by its lack of acetylenic constituents.

This work is part of a chemotaxonomic investigation of the genus *Dahlia*. Further data concerning the *Dahlia* species will appear in a forthcoming publication. The original plants were collected in Mexico during the autumn of 1958 and were propagated in the Botanical Garden of Aarhus during the summer of 1964.*

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* All the examined species are available as herbarium specimens at The Botanical Institute, University of Aarhus and at The Botanical Garden, Copenhagen.