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ACETYLENES IN THE GENUS *DAHLIA*, ASTERACEAE

IN HONOUR OF PROFESSOR G. H. NEIL TOWERS 75TH BIRTHDAY

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Key Word Index—*Dahlia* species, acetylenes, Coreopsedinae, Heliantheae, Asteraceae.

Abstract—*Dahlia* species grow wild in several places of Mexico. A series of *Dahlia* species have been propagated in Denmark and some of these plants have been studied at the Chemical Institute, University of Aarhus in Denmark. More than 40 compounds have been characterized after isolation from roots and tubers or from aerial plant material. The major compounds were acetylenes that occur in these *Dahlia* species and other genera of Heliantheae, a tribe within Asteraceae. *Dahlia merckii* Lehm is unique both chemically and in terms of its chromosome number, whereas *Dahlia tubulata* is also unique in the chemical sense that it contains many thiophene compounds some of which are acetylenes, a new discovery among the *Dahlia* species.

INTRODUCTION

Various *D. coccinea* strains and other species of the genus *Dahlia* have been obtained from the Botanical Garden of Copenhagen, where the plants have been propagated from seeds collected from plants in Mexico by the Danish botanist J. P. Hjerting and his two colleagues R. Lester and J. G. Hawkes in 1958. Although the genus *Dahlia* originally grew wild in Mexico, a few *Dahlia* species are however growing wild in Guatemala.

The *D. coccinea* strains from Mexico were of different colour and ploidy. All *Dahlia* plants treated were subjected to investigation of: 1) roots and tubers; 2) stems and leaves and 3) flowerheads, respectively.

The acetylenes were isolated during the years 1964 to 1992 [1–10]. A large number of *Dahlia* plants belonging to the subgroup Coreopsedinae, Heliantheae, Asteraceae were investigated at the Chemical Institute, University of Aarhus, Denmark.

The solvent used for the tuber extractions was diethyl ether or a mixture of diethyl ether and light petroleum (b.p. below 50°). For the aerial parts (leaves and stems, and flowerheads) light petroleum was used in order to get an extract almost free from chlorophyll.

Determination of chromosome numbers was carried out for a series of *Dahlia* species by Dr. Peter Jacobsen, Copenhagen. Two of the *D. coccinea* strains were diploid ($2n = 32$) and two others were tetraploid ($2n = 64$). *D. merckii* Lehm (formerly anticipated to be *D. scapigera* (A. Dietr.) Linked et Otto var. *scapigera* forma merckii (Lehm) is an aneuploid *Dahlia* with the chromosome number $n = 18$ and its chemical deviation from other *Dahlia* species makes it unique. Interestingly *Dahlia tubulata* has a chromosome number of $n = 16$ [11].

Dahlia tubulata P. D. Sorensen [10] is also unique because of its sulfur compounds, which have not been observed in any other *Dahlia* species.

Sulfur compounds isolated from this species are not usual for the genus *Dahlia*, whereas comparable sulfur compounds are known to be present in the genera *Coreopsis* and *Bidens* which are closely related to the genus *Dahlia* in the subgroup Coreopsedinae.

To date more than twenty-five *Dahlia* species from various localities in Mexico have been investigated as described by *Lam* and *Hansen* [12].

Additionally several isolated compounds were provided to Professor G. H. N. Towers at the University of British Columbia for determination of their biological activities about 1976.

RESULTS AND DISCUSSION

The most common polyacetylenes occurring in a *Dahlia* species are listed below. Some were biologically active when tested against mosquito larvae, nematodes and blackfly larvae, and they have also been shown to be phototoxic to certain freshwater algae [13–15].

"Survival" of acetylenes

Very often the question has been put: How can highly unsaturated compounds persist in plants,

The most prominent acetylenes of *Dahlia coccinea* Cav.
(1422) (scarlet)

$$R-CH\overset{E}{=}CH-(C\equiv C)_4-CH=CH_2$$

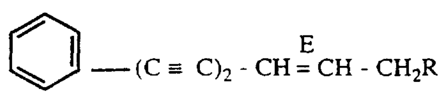
1) $R=CH_3$, 2) $R=CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3$, 3) $R=CH_2OH$, 4) $R=CHO$

$$R-CH\overset{E}{=}CH-(C\equiv C)_3-CH\overset{E}{=}CH-CH=CH_2$$

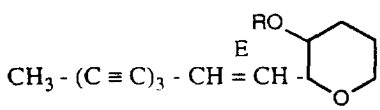
1) $R=CH_3$, 2) $R=CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3$, 3) $R=CH_2OH$, 4) $R=CHO$

cf. Biochemical Systematics Vol. 1, pp. 83–86, 1973.

The most prominent acetylenes of yellow *Dahlia coccinea*
(2n = 64)



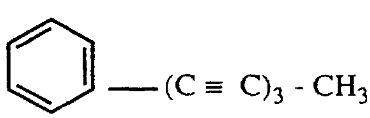
1) $R=H$, 2) $R=OH$, 3) $R=-O-\overset{O}{\overset{\|}{C}}-CH_3$

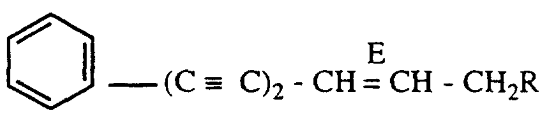


1) $R=H$, 2) $R=-\overset{O}{\overset{\|}{C}}-CH_3$

cf. Phytochemistry Vol. 7, pp. 269–275, 1968.

The most prominent acetylenes of *Dahlia pinnata*





1) $R=H$, 2) $R=-O-\overset{O}{\overset{\|}{C}}-CH_3$

cf. Phytochemistry Vol. 8, pp. 1021–1024, 1969.

The most characteristic acetylenes of *Dahlia australis* are:

$$HO-CH_2-CH\overset{E}{=}CH-(C\equiv C)_4-CH=CH_2$$

$$CH_3-CH\overset{E}{=}CH-(C\equiv C)_2-(CH\overset{EE}{=}CH)_2-\underset{\substack{|\\R^1}}{CH}-CH_2-CH_2-R^1$$

$$R^1=R^2=-O-\overset{\overset{O}{\|}}{C}-CH_3$$

$$-(C\equiv C)_2-CH\overset{E}{=}CH-R$$

$$1)\ R=CH_3,\ 2)\ R=CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3,\ 3)\ R=CH_2OH$$

cf. Phytochemistry Vol. 30, pp. 515–518, 1961.

The most prominent acetylenes of *Dahlia tenuicaulis*

$$R-CH\overset{E}{=}CH-(C\equiv C)_4-CH=CH_2$$

$$1)\ R=CH_3,\ 2)\ R=CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3,\ 3)\ R=CHO$$

$$R-CH\overset{E}{=}CH-(C\equiv C)_3-CH\overset{E}{=}CH-CH=CH_2$$

$$1)\ R=\ CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3,\ 2)\ R=CHO$$

cf. Phytochemistry Vol. 10, pp. 2227–2228, 1971.

The most prominent acetylenes of *Dahlia rudis*

$$R-CH\overset{E}{=}CH-(C\equiv C)_4-CH=CH_2$$

$$1)\ R=CH_3,\ 2)\ R=CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3,\ 3)\ R=CH_2OH,\ 4)\ R=CHO$$

$$R-CH\overset{E}{=}CH-(C\equiv C)_3-CH\overset{E}{=}CH-CH=CH_2$$

$$1)\ R=CH_3,\ 2)\ R=CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3,\ 3)\ R=CH_2OH$$

cf. Biochemical Systematics, Vol. 1, pp. 83–86, 1973.

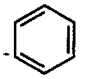
The most prominent acetylenes of *Dahlia sherffii* (1235)

$$R-CH\overset{E}{=}CH-(C\equiv C)_4-CH=CH_2$$

1) $R=CH_3$

$$R-CH\overset{E}{=}CH-(C\equiv C)_3-CH\overset{E}{=}CH-CH=CH_2$$

1) $R=CH_3$, 2) $R=CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3$

$R-CH\overset{E}{=}CH-(C\equiv C)_2-$ 

1) $R=CH_3$, 2) $R=CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3$, 3) $R=CH_2OH$, 4) $R=CHO$

cf. Biochemical Systematics, Vol. 1, pp. 83–86, 1973.

The most prominent acetylenes of *Dahlia merckii*

$$CH_3-CH\overset{E}{=}CH-CH\overset{E}{=}CH-C\equiv C-CH\overset{E}{=}CH-CH\overset{E}{=}CH-(CH_2)_4-CH=CH_2$$

$$CH_3-CH\overset{E}{=}CH-(C\equiv C)_2-CH\overset{E}{=}CH-CH\overset{E}{=}CH-(CH_2)_4-CH=CH_2$$

$$CH_3-(CH\overset{EE}{=}CH)_2-C\equiv C-(CH\overset{EE}{=}CH)_2-(CH_2)_n R,\ n=2\text{-}5;$$

$n=2,3,5$; $R=-O-\overset{\overset{O}{\|}}{C}-CH_3$; $n=3,5$; $R=OH$; $n=2,4$; $R=CHO$

$$CH_3-CH\overset{E}{=}CH-(C\equiv C)_2-CH\overset{E}{=}CH-\underbrace{CH-CH}_{O}-(CH_2)_3-O-\overset{\overset{O}{\|}}{C}-CH_3$$

$$CH_3-CH\overset{E}{=}CH-(C\equiv C)_2-(CH\overset{EE}{=}CH)_2-(CH_2)_n R,\ n=3,5;\ R=OH$$

cf. Phytochemistry Vol. 31, pp. 2743–2745, 1992 and Phytochemistry Vol. 31, 4353–4354, 1992.

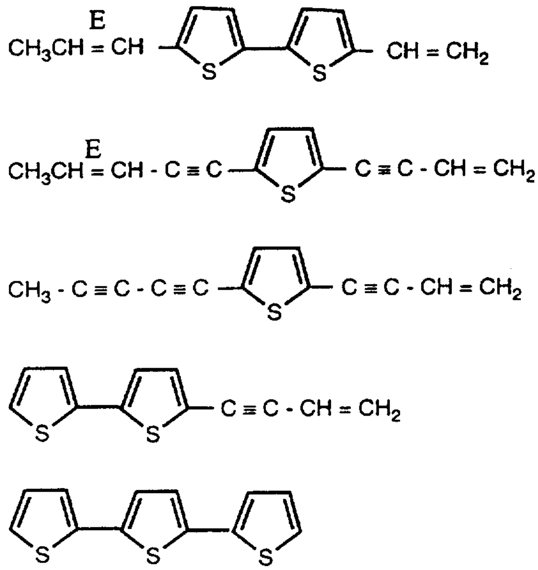
which are known to be decomposed very rapidly, when exposed to ultraviolet light? Previously we have noticed that polyaromatic hydrocarbons like pyrene, anthracene and other polyaromatic hydrocarbons were decomposed (discoloured) on *tlc*-plates covered with silica, when exposed to ultraviolet light within a few hours, whereas the same aromatic hydrocarbons, when applied to *tlc*-plates covered with silica admixed 5 to 10 per cent of caffeine were stabilized and did not decompose even after a long time (unpublished results). Suggesting that caffeine has a stabilizing effect. The π-electrons may interact with π-electrons in other compounds, an effect that has also been noticed to be valid for polyacetylenes and other π-electron-rich compounds like thiophenes [16]. Indeed, many experiments were carried out in order to prove that the π-electrons have the ability to interact with π-electrons in other compounds. A selected series of compounds either related to caffeine (8-chlorocaffeine, uric acid and 1,3,7,9-tetramethyluric acid) or compounds often found in nature have been added to silica one by one and *tlc*-plates were produced.

A selected series of highly unsaturated compounds isolated from *Dahlia* species and from other plants of Asteraceae were applied to the above mentioned *tlc*-plates and after a certain time of irradiation in daylight (ultraviolet light) the percent of recovery could be determined and hence providing a measure of the effect of stabilization against irradiation. It is not meant to be an exact determination, but with a great number of attempts pointing to the same direction and with caffeine as a controlling agent it seems to be a fairly good explanation for the relative stabilization of polyacetylenes and other unsaturated compounds as long as they are in the plants, where several aromatic compounds, purines and chlorophylls, are pre-

The most prominent acetylenes of *Dahlia tubulata*

$$R-CH=CH-(C\equiv C)_4-CH=CH_2$$

$$1)\ R=CH_3,\ 2)\ R=CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3$$



cf. Phytochemistry Vol. 29, pp. 3153–3154, 1990.

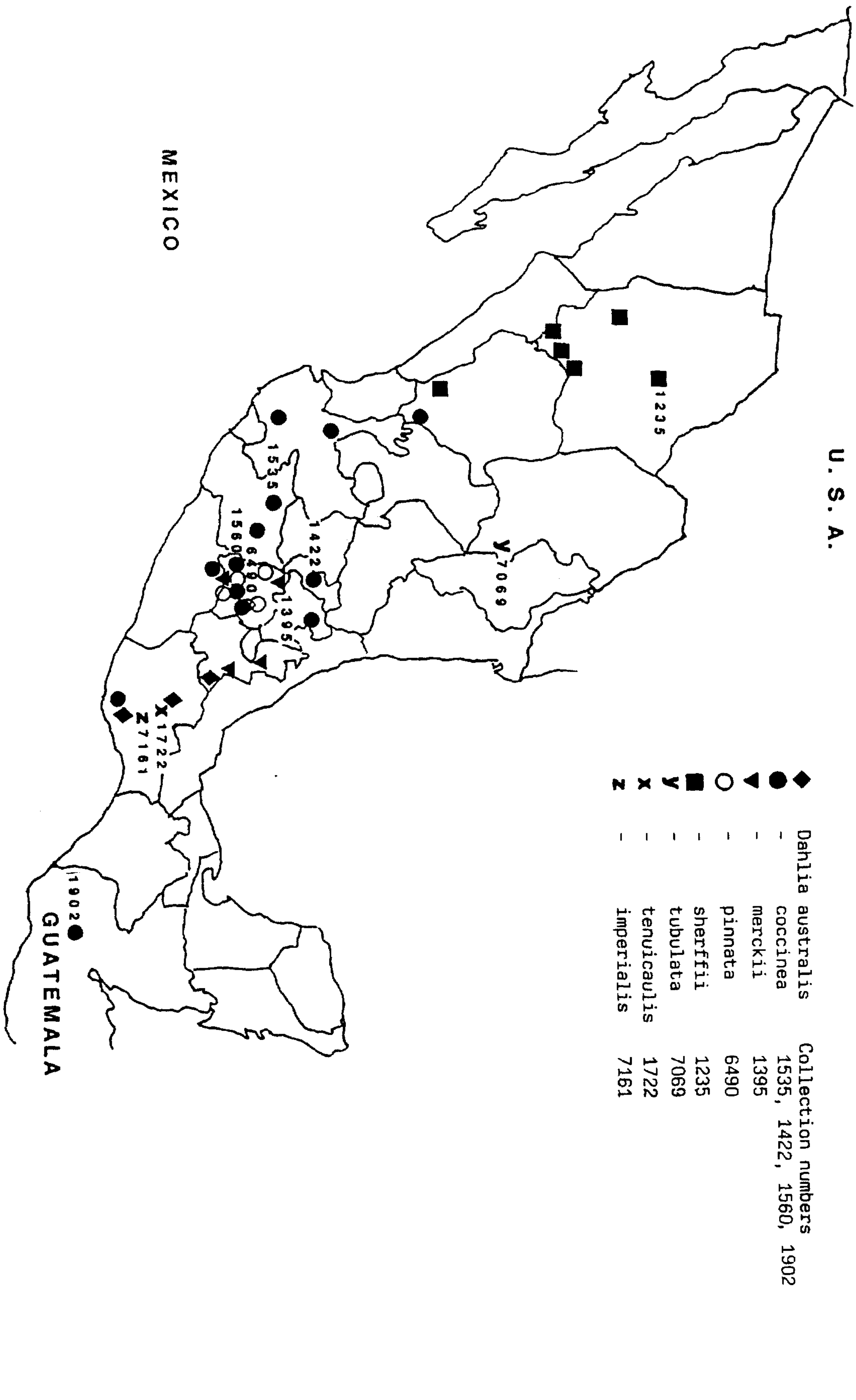
sent to stabilize the highly unsaturated compounds like polyacetylenes and other compounds by π-electron interactions [17].

In the pure state or in solution many of the polyacetylenes and related compounds are known to exert a high grade of phototoxicity. If it is possible to stabilize to some extent the often very active polyacetylenes with naturally occurring substances or with degradable synthetic products, that will exert a loose interaction, there should be basis for a commercial production of biologically active and stabilized but still bio-degradable pesticides.

Localities in Mexico where *Dahlia* species have been collected in 1958 by J. G. Hawkes, J. P. Hjertling and R. Lester.

Numbers	Collection
1235	*D. sherffii* Sörensen (formerly D. pinnata (det. D. Philcox)) Mexico, Chihuahua State (Pilares de) Majalca, 40 miles northwest of Chihuahua, August 14, 1958. Alt.: 2100 m. Flowers magenta-pink, discs yellow.
1395	D. *merckii Lehm*, Mexico State, new highway 57 from Mexico City to San Juan del Rio at 167 km, near Calpulalpan, San Martin, September 4, 1958. Alt.: 3100 m. Flowers pink.
1422	*D. coccinea* Cav Mexico, Queretaro State, road from San Juan del Rio-Queretaro Highway north to Bernal, Cerro Galeras, east of road, September 5, 1958. Alt.: 2050 m. Flowers flame-coloured.
1535	*D. coccinea* Cav Mexico, Michoacan State, near Chilchota, road from Morelia to Guadalajara between Carapan and Tanguancicuraro, September 21, 1958. Alt.: 1600 m. Flowers scarlet.
1560	*D. coccinea* Cav Mexico, Michoacan State, near Morelia, Cerro Punguato, September 26, 1958. Alt.: 2200 m. Flowers yellow.
1722	*D. tenuicaulis* Sšrensen Mexico, Oaxaca State, Sierra de Juarez, road from Oaxaca to Ixtlan de Juarez, 13.5 miles from Oaxaca-Tehuantepec highway, October 21, 1958. Alt.: 2700 m Damp oak forests. Stem woody. Flowers magenta.

Collections have been carried out later by J. P. Hjerting in 1983, 1984 and 1988.


MEXICO
U. S. A.
GUATEMALA
◆ – Dahlia australis
● – coccinea
▼ – merckii
○ – pinnata
■ – sherffii
Y – tubulata
X – tenuicaulis
Z – imperialis
Collection numbers
1535, 1422, 1560, 1902
1395
6490
1235
7069
1722
7161

Dahlia seeds obtained from professor Dr. Paul Sörensen in Illinois (1970) have been propagated in the botanical garden of Copenhagen by J. P. Hjerting.

6490 *D. pinnata*. Seeds collected 1.5 miles north of Villa Guerrero, Mexico State, September 1966.

Acknowledgements—For the collection and propagation of the *Dahlia* plants Dr. J. P. Hjerting is cordially acknowledged. The great botanical assistance carried out by J. P. Hjerting and H. V. Hansen at the botanical garden of Copenhagen is highly appreciated and the close collaboration between Dr. Hjerting and Dr. Paul Sörensen has been of great value for the verification of the plant material. Mrs. Annette T. Larsen, Chemical Institute, University of Aarhus, is thanked for the printing of this publication.

REFERENCES

1. Lam, J., Kaufmann, F. and Bendixen, O., *Phytochemistry*, 1968, 7, 269.
2. Bendixen, O., Lam, J. and Kaufmann, F., *Phytochemistry*, 1969, **8**, 1021.
3. Kaufmann, F. and Lam, J., *Acta Chemica Scandinavica*, 1965, **19**, 1267.
4. Lam, J., *Phytochemistry*, 1971, **10**, 2227.
5. Sörensen, P. D., Thesis about systematics of the genus Dahlia (Coreopsedinae, Heliantheae). The University of Iowa 1967.
6. Lam, J., *Biochemical systematics* (*now Biochemical Systematics Ecology*), 1973, **1**, 83.
7. Lam, J. and Kaufmann, F., *Phytochemistry*, 1971, **10**, 1877.
8. Neushield, K., Christensen, L. P. and Lam, J., *Phytochemistry*, 1992, **31**, 2743 and 4353.
9. Lam, J., Christensen, L. P. and Thomasen, T., *Phytochemistry*, 1991, **30**, 515.
10. Christensen, L. P., Lam, J. and Thomasen, T., *Phytochemistry*, 1990, **29**, 3153.
11. Hansen, H. V. and Hjerting, J. P., *Nordic Journal of Botany*1996, **16**(4), 445.
12. Lam, J. and Hansen, L., in *Methods in Plant Biochemistry*, Vol 4, chapter 6, ed. J. L. Harwood and J. R. Bowyer, Academic Press, 1990, p. 159.
13. Wat, C.-K., Prasad, S. K., Graham, E. A., Partington, S., Arnason, T., Towers, G. H. N. and Lam, J., *Biochemical Systematics Ecology*, 1981, **9**, 59.
14. Arnason, T., Stein, J. R., Graham, E., Wat, C.-K., Towers, G. H. N. and Lam, J., *Canadian Journal of Botany*, 1981, **59**, 54.
15. McLachlan, D. and Arnason, T., Lam, J., *Biochemical Systematics Ecology*, 1986, **14**, 17.
16. Lam, J., *Planta Medica*, 1973, **24**, 107.
17. Lam, J. and Thomasen, T. in *Chemistry and Biology of Naturally Occurring Acetylenes and Realted Compounds* (*NOARC*), ed. J. Lam, H. Breteler, T. Arnason L. and Hansen. The Series of Bioactive Molecules, Vol 7. Elsevier, 1988.