Phytochemistry, 1969, Vol. 8, pp. 1021 to 1024. Pergamon Press. Printed in England.

SHORT COMMUNICATION

POLYACETYLENES OF *DAHLIA PINNATA**

OTTO BENDIXEN, JØRGEN LAM and FRANTZ KAUFMANN†

Chemical Institute, University of Aarhus, 8000 Århus C, Denmark

(*Received* 7 *December* 1968)

Abstract—*Dahlia pinnata* Cav. was examined for polyacetylenes. The resulting data have been compared to those for six strains of *D. coccinea* Cav. and some differences were established. Compounds with an ene-diyne-diene chromophore are abundantly represented in *D. pinnata*, whereas at most traces of compounds with this chromophore were detected in *D. coccinea*.

INTRODUCTION

SINCE the horticultural varieties of *Dahlia* (Compositae) seem to be derived from *Dahlia coccinea* Cav. and *D. pinnata* Cav., a chemical investigation of these two species may be of taxonomic value. Six strains of *D. coccinea* have been investigated previously for their acetylenic contents.[1,2] The present publication deals with the polyacetylenes of *D. pinnata* Cav.

DISCUSSION AND RESULTS

The acetylenes isolated from the lipophilic extracts of *Dahlia pinnata* are listed in the Table. This dahlia, compared with the six *D. coccinea* strains previously examined, shows a general difference and also a resemblance in the acetylenic pattern. As seen from the table the tubers generally contain acetylenes in great abundance, while the aerial parts only contain acetylenes in small amounts and the number of compounds is rather restricted.

The ene-tetrayne-ene (II) and the ene-triyne-ene (V) are present in small quantities in *D. pinnata* as well as in all the *D. coccinea* strains[1] and *D. scapigera* Link et Otto.[3] These compounds are widely distributed in the tribe Heliantheae.[4] As to the phenyl-diyne-ene compounds (XIV), (XV), (XVI), and (XVII), *D. pinnata* is very similar to one of the *D. coccinea* strains.[1]

The diacetate (XII) and the diol (XIII) are fairly abundantly represented in *D. pinnata* whereas compounds with the same chromophore were detected in *D. coccinea* only as traces in two strains. These compounds have also been isolated by Fairbrother[5] and by Safe[2,6] from the tubers of a number of horticultural dahlia hybrids.

* Part IV in the series "Chemical Constituents of the Genus *Dahlia*"; for part III, see Ref. 1.

† Present address: A/S Grindstedværket, 8000 Århus C.

[1] J. LAM, F. KAUFMANN and O. BENDIXEN, *Phytochem.* 7, 269 (1968).
[2] E. R. H. JONES, *Chem. Britain* 6 (1966).
[3] F. KAUFMANN and J. LAM, *Acta Chem. Scand.* **19**, 1267 (1965).
[4] N. A. SÖRENSEN, *Chemical Plant Taxonomy* (edited by T. SWAIN), p. 219, Academic Press, London (1963).
[5] J. F. R. FAIRBROTHER, Thesis, University of Oxford (1965).
[6] S. H. SAFE, Thesis, University of Oxford (1965).

TABLE 1. *Dahlia pinnata* ACETYLENES

		Fresh material			
		Tubers (mg/kg)	Leaves (mg/kg)	Flowers (mg/kg)	Reference
I	CH_3—[C≡C]$_5$—CH=CH_2	*t**	*t**		12
II	CH_3—CH=CH—[C≡C]$_4$—CH=CH_2	1	0·6	1	16
III	CH_3—[C≡C]$_4$—CH=CH—CH=CH_2	0·5	0·5	4	17
IV	CH_3—[C≡C]$_3$—[CH=CH]$_2$—[CH_2]$_4$—CH=CH_2		13	10	5, 6, 11
V	CH_3—CH=CH—[C≡C]$_3$—CH=CH—CH=CH_2	3	2	3	18
VI	CH_3—[C≡C]$_3$—[CH=CH]$_2$—CH(OAc)—CH_2—CH_2OAc	27	*t**	*t**	1, 2, 7, 19
VII	CH_3—[C≡C]$_3$—[CH=CH]$_2$—CH(OH)—CH_2—CH_2OH		*t**	*t**	1, 8
VIII	 —[C≡C]$_3$—CH_3	24			9
IX	 —[C≡C]$_3$—CH_2OAc	*t**			10
X	CH_3—CH=CH—[C≡C]$_2$—[CH=CH]$_2$—CH=CH_2	1·2			16
XI	CH_3—CH=CH—[C≡C]$_2$—CH=CH—CH(OAc)—CH(OAc)—CH=CH_2	8			2, 5
XII	CH_3—CH=CH—[C≡C]$_2$—[CH=CH]$_2$—CH(OAc)—[CH_2]$_2$—OAc	71			2, 13
XIII	CH_3—CH=CH—[C≡C]$_2$—[CH=CH]$_2$—CH(OH)—[CH_2]$_2$—OH	53			2, 13
XIV	 —[C≡C]$_2$—CH=CH—CH_3	244			9
XV	 —[C≡C]$_2$—CH=CH—CHO	8			1, 14, 15
XVI	 —[C≡C]$_2$—CH=CH—CH_2OAc	100			16
XVII	 —[C≡C]$_2$—CH=CH—CH_2OH	43			15

* *t* means amounts less than 0·02 mg.

The diacetate (VI) was determined in the tubers of one *D. coccinea* strain and in the leaves of another *D. coccinea* in this laboratory.[3] Furthermore it is recorded by C. G. Chin to be present in the tubers of a *D. coccinea*[2,7] and in a horticultural dahlia by Safe.[6]

In the upper parts of *D. pinnata* acetylenic hydrocarbons dominate and there are only traces of oxygen-containing compounds. The hydrocarbons I–III and V are present in both the tubers and the upper parts, while the hydrocarbon IV was isolated from the aerial parts only. This compound was not detected in *D. coccinea*, but it was found by Fairbrother[5] and Safe[6] in the upper parts of horticultural dahlia hybrids. The oxygenated compounds from the upper parts of *D. pinnata* show u.v. spectra corresponding to a triyne-diene chromophore as in the diacetate (VI) and the diol (VII). They have R_f values (TLC) in agreement with those of the authentic compounds.

Furthermore, in the tubers of *D. pinnata*, traces of two compounds each showing an ene-diyne-diene chromophore were detected. The compounds seem to be partly hydrolysed diacetate (XII) derivatives:

$$CH_3—CH=CH—[C\equiv C]_2—[CH=CH]_4CH(OR')\cdot[CH_2]_2\cdot OR''$$

(XVIII) $R'=H$, $R''=COCH_3$

(XIX) $R'=COCH_3$, $R''=H$

Too limited amounts were present for a reliable determination of these compounds.

EXPERIMENTAL

Material

Dahlia pinnata (det D. Philcox) was collected 10 August 1958 in Mexico, Chihuahua State, 40 miles north-west of Chihuahua (Pilares de), Majalca, 2100 m, by J. G. Hawkes, J. P. Hjerting, and R. Lester and brought to Denmark by J. P. Hjerting. The plant has since been propagated in the Botanical Gardens of Copenhagen and Aarhus, and herbarium material is deposited at the Botanical Institute, University of Aarhus. The chromosome number $2n=64$ (tetraploid) was determined by Dr. Peter Jacobsen, Copenhagen.

Chemical Investigation

The tubers, leaves, and flower heads were examined separately. Immediately after harvesting, the flowering plants were minced and extracted, first with petroleum ether and eventually with ether. The extracts were dried (Na_2SO_4) and the solvent evaporated. Each of the lipophilic residues were chromatographed on silica gel columns eluted with petroleum ether containing increasing amounts of ether, and finally with pure ether. Finally, the column was eluted with methanol. Some of the compounds were thus obtained in a sufficiently pure state for spectroscopic identification. Those which were not were purified by rechromatography either

[7] C. G. CHIN, Thesis, University of Oxford (1965).
[8] F. BOHLMANN, C. ARNDT, K. M. KLEINE and H. BORNOWSKI, *Chem. Ber.* **98**, 155 (1965).
[9] J. S. SÖRENSEN and N. A. SÖRENSEN, *Acta Chem. Scand.* **12**, 765 (1958).
[10] F. BOHLMANN, H. BORNOWSKI and K. M. KLEINE, *Chem. Ber.* **97**, 2135 (1964).
[11] F. BOHLMANN, E. INHOFFEN and P. HERBST, *Chem. Ber.* **90**, 124 (1957).
[12] J. S. SÖRENSEN, D. HOLME, E. T. BORLAUG and N. A. SÖRENSEN, *Acta Chem. Scand.* **8**, 1769 (1954).
[13] F. BOHLMANN, S. KÖHN and C. ARNDT, *Chem. Ber.* **99**, 3433 (1966).
[14] J. LAM and F. KAUFMANN, *4th Internat. IUPAC Symp. on the Chemistry of Natural Products*, Stockholm 1966, section paper 4–21.
[15] F. BOHLMANN, S. KÖHN and E. WALDAU, *Chem. Ber.* **99**, 3201 (1966).
[16] J. S. SÖRENSEN and N. A. SÖRENSEN, *Acta Chem. Scand.* **8**, 1741 (1954).
[17] F. BOHLMANN, K. M. KLEINE and C. ARNDT, *Chem. Ber.* **97**, 2125 (1964).
[18] F. BOHLMANN, S. POSTULKA and J. RUHNKE, *Chem. Ber.* **91**, 1631 (1958).
[19] F. BOHLMANN and K. M. KLEINE, *Chem. Ber.* **97**, 1193 (1964).

by column or by preparative TLC. For characterization, u.v., i.r. and NMR data were used and the compounds were compared with authentic reference materials by TLC (silica gel).

Acknowledgements—The authors wish to thank Dr. J. P. Hjerting, Botanical Gardens, Copenhagen, for the plant material, Professor K. Larsen, Botanical Institute, University of Aarhus, and Mr. J. Knudsen, cand. hort., Botanical Gardens, Aarhus, for propagation of the material, and Dr. P. Jacobsen, Copenhagen, for the determination of the chromosome number.