Phytochemistry, 1975, Vol. 14, pp. 1621–1623. Pergamon Press. Printed in England.

FLAVONOIDS AND POLYACETYLENES IN *DAHLIA TENUICAULIS**

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(*Received* 4 *November* 1974)

Key Word Index—*Dahlia tenuicaulis*; Compositae; flavanoids; chalcones; flavan-4-ol; polyacetylenes.

Abstract—5,7,4′-Trimethoxyflavanone, 5-hydroxy-7,4′-dimethoxyflavanone, 2′-hydroxy-4,4′,6′-trimethoxychalcone, and a new naturally occurring compound, 5,7,4′-trimethoxyflavan-4-ol have been isolated from the leaves of *Dahlia tenuicaulis* Sorensen. Two chalcones, 4,2′,4′-trihydroxychalcone and 3,2′,4′-trihydroxy-4-methoxychalcone, and 5-hydroxy-7,4′-dimethoxyflavanone have been isolated from the flower heads. Minute amounts of the polyacetylene 1,3-diacetoxy-tetradeca-4,6-diene-8,10,12-triyne have been found in both leaves and flower heads, whereas 1-acetoxy-tetradeca-4,6-diene-8,10,12-triyne was present only in the flower heads.

INTRODUCTION

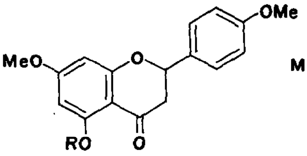
A previous investigation [1] of the leaves of *Dahlia tenuicaulis* Sorensen (*D. lehmanni* Hieron.) for acetylenic substances showed that only minute amounts were present. The compound (**1**) was, however, fully characterized and its structure verified by synthesis [1]. Six acetylenic compounds, however, were later isolated from the roots of *D. tenuicaulis* [2]. This paper describes the isolation of five flavonoids (**2**–**6**) and two more acetylenes (**7** and **8**) from the leaves and flowers.

DISCUSSION AND RESULTS

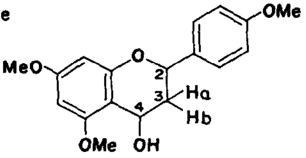
Although compound **1** has been described previously it should be noted that both it and the corresponding chalcone are rapidly destroyed by treatment with sodium methoxide in methanolic solution (Table 1).

Reinvestigation of leaves collected in autumn revealed the presence of **2** (mp 115·5–115·9°). This compound was present in higher amounts than in leaves collected in the winter or the spring. It was found in trace amounts only in the flowers of specimens collected in March. The NMR spectrum showed good agreement with that of naringenin-4′,7-dimetylether (**2**) [5]. The UV spectra [4] indicate a hydroxy group in position 5 (Table 1) and MS data are consistent with **2** (Table 2).

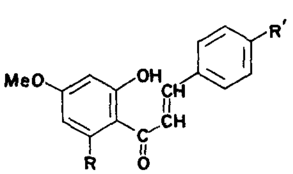
The spectral data of the chalcone **4** were in good agreement with those for the synthetic product (Tables 1 + 2). The other two chalcones (**5** and **6**) were isolated from the flower heads, and



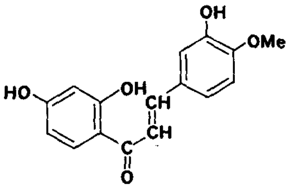
(**1**) R = Me
(**2**) R = H



(**3**)



(**4**) R = R′ = OMe
(**5**) R = H; R′ = OH



(**6**)

(**7**) $Me-(C\equiv C)_3-(CH\overset{tt}{=}CH)_2-CH(OAc)-CH_2-CH_2OAc$
(**8**) $Me-(C\equiv C)_3-(CH=CH)_2-(CH_2)_2-CH_2OH$

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* Part 6 in the series "Chemical Constituents of the Genus *Dahlia*".

Table 1. UV absorption spectral data of the flavonoids λ_{max} (nm)

Compounds	MeOH	MeOH + NaOMe	MeOH + $AlCl_3$	MeOH + $AlCl_3$ + HCl	MeOH + NaOAc	MeOH + NaOAc + H_3 BO_3
1	230 284	*	230 283	230 283	230 283	230 283
2	289	289 360	314	311	289	289
3	275 (281)	275 (281)	275 (281)	275 (281)	275 (281)	275 (281)
4	(308) 366	*	252 410	(244) 395	364	295 372
5	240 372	252 432	334 428	(332) 422	280 408	280 408
6	263 (310) 378	418	274 435	270 426	263 394	264 394

Figures in parentheses indicate inflections.
* Appearance of a new band at 328 nm because of destruction.

were identified mainly on the basis of their UV, NMR and MS spectra [4] (Tables 1 and 2). 4,2′,4′-trihydroxychalcone (**5**) was previously isolated from *Dahlia variabilis* [6]. Chalcone **5** is 4-methoxybutein; butein itself has also been isolated from *Dahlia variabilis* [7].

A new compound (**3**) was isolated from the petrol extract of the leaves. Its UV spectrum had a λ_{max} at 275 nm with an inflection at 281 nm. The NMR and MS spectral data suggested a flavan-4-ol and this was confirmed by mild oxidation to the flavanone (**1**) (see Experimental). Several synthetic products have been prepared in the study of the stereochemistry of the flavan-4-ols [8–10]. The isolated compound (**3**) is believed to have the B-ring in an equatorial position and the OH-group in a trans-position relative to it in agreement with the results reported by Lillya *et al* [9]. Another flavan-4-ol, luteoforol (4,5,7,3′,4′-pentahydroxyflavan) is known from *Sorghum vulgare* L. [11] and strawberry leaves [12].

Table 2. MS data for compounds **1**–**6**. The most prominent peaks (percentage relative intensities) of the fragmentation pattern are listed

	1	**2**	**3**	**4**	**5**	**6**
120					85	
121	100	48	30	84		
134	74	100	100	100		
137					100	100
150						55
163					18	18
166		24				
180	28			66		
181	72		26			
191			55			
193		17				
207	32			42		
256					28	
267			15			
283			16			
286						13
297			61			
298			64			
299		21				
300		40				
313	29			24		
314	50			35		
316			1			

Since fresh plant material was extracted cautiously with light petroleum and subsequently with ether at room temperature it is very likely that the compounds isolated and characterized are present in free (non-glycosidic) state. Glycosides of similar chalcones and flavanones are reported to be present in *Dahlia* species and other members of the section Coreopsedinae belonging to the tribe Heliantheae (Compositae) [13].

EXPERIMENTAL

The first polyacetylene (**7**) was shown to be present in extracts of the leaves and the flower heads by UV spectra, but was present in too small amounts for full characterization. However, comparison with authentic **7** by TLC and MS supported the proposed structure. The corresponding diol, formed on hydrolysis, with one alcohol group in the allylic position, was readily oxidized with activated manganese dioxide to the ketone [3]. The latter gave an UV spectrum with displaced maxima corresponding to an extended chromophore due to the carbonyl group in conjugation with the triyne-diene system [4].

The second polyacetylene was found only in the flower heads. The UV spectrum exhibited a triyne-diene chromophore, but the compound occurred in too small amounts to permit definite identification. However, TLC comparison with (**8**) showed good agreement. The fact that these two polyacetylenes (**7** and **8**) have been isolated from other dahlia species [4] supports their presence in *D. tenuicaulis*. The petrol fraction of the leaves gave three flavonoids (**1**–**3**) and the ether extract contained one extra compound (**4**). Two other chalcones (**5**,**6**) were isolated from the flowers. The presence of trimethylnaringenin (**1**) was confirmed [1] and its UV and MS data are given in Tables 1 and 2.

Since this dahlia species does not flower during the summer in Denmark, the plants were kept in a greenhouse, at Aarhus Botanical Gardens, it then being possible to collect a few flowers in Dec. and Jan. 39 g (fr. wt) of flower heads were collected for extraction with petrol and subsequently with Et_2O. Leaves were extracted similarly.

The flavanones **1** and **2** and the polyacetylenes were present in the petrol extracts, whereas the chalcones were found in the ether extracts. The flavan-4-ol was present in the petrol extract from the leaves.

The NMR data were obtained from $CDCl_3$ solns of the compounds. For compound **3** the following NMR data were obtained: δ 6·12 (*m*, A-ring), 6·92 and 7·40 (two *d*, *J* 8 cps, B-ring), 3·74 (*s*, Me–O–), 3·80 (*s*, Me–O–), 3·84 (*s*, Me–O–), 5·10 (*dd*, *J* 11 and 3·2 cps, H at C-2), 4·98 (*dd*, *J* 4 and 2·5 cps, H at C-4), 1·98 (*ddd*, *J* 15, 11 and 4 cps, H at C-3a), 2·22 (*ddd*, *J* 15, 3·2 and 2·5 cps, H at C-3b).

The MS were obtained by direct inlet MS. The compounds **1–6** were subjected to various reactions described [5] (Table 1). Only **3** could not be identified in this way. On addition of conc. HCl or H_2SO_4 to a methanolic soln of **3** the soln immediately became deep purple to mauve in good agreement with the reactions described for luteoforol and a synthetic 4-hydroxy-5,7,4′-trimethoxyflavan [14]. This can be used as a rapid test for **3**: separation on Si gel sprayed with conc HCl gives a permanent red–violet spot, whereas the compounds **1–5** remain colourless or give yellow–brown spots. Oxidation with activated MnO_2 [3] (2 hr) gave the corresponding flavanone (**1**), (IR,UV) separated on TLC (Si gel) from unreacted 4-hydroxyflavan. The oxidation proceeds more slowly than is the case for the acetylenic diol obtained by hydrolysis of **7**.

Acknowledgements—The authors wish to thank Mrs. Tove Thomasen for technical assistance during the laboratory examinations and Dr. S. Jagner for linguistic criticism.

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