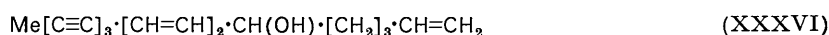
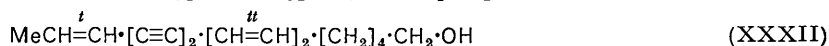
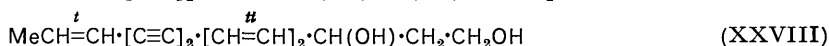
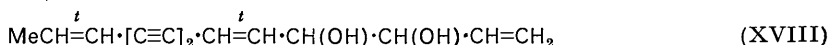


## Natural Acetylenes. Part XLIX.<sup>1</sup> Polyacetylenes from *Dahlia scapigera* (A. Dietr.) Link and Otto var. *scapigera* f. *scapigera* and Some *Dahlia* Hybrids<sup>2</sup>

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Examination of the above *Dahlia* species revealed the presence of 8 polyacetylenic compounds of which the C<sub>16</sub> ene-diyne-ene alcohol (XXXII) and its acetate were new. In representatives of the main garden varieties 36 poly-



acetylenes were detected, including the new (XVIII), (XXVIII), and (XXXVI) and their acetates. Seasonal variations of the content were noted. The C<sub>17</sub> alcohol (XXXVI) and the C<sub>16</sub> alcohol (XXXII) were synthesised; the latter and the corresponding C<sub>14</sub> compound by novel routes.

A PRELIMINARY account of the work concerned with the polyacetylene content of species and garden varieties belonging to the genus *Dahlia* (Compositae) carried out in this department was given some years ago,<sup>3</sup> and part of the work was published in full.<sup>4</sup> This paper deals with the remainder of the unpublished information; in the first place with the new compounds found. All the polyacetylenes identified are listed in the Table: their abundance and source are indicated, and the actual concentrations detected are quoted in the Experimental section. Of the polyacetylenes detected in *D. coccinea*,<sup>4</sup> only the C<sub>17</sub> ene-diyne-diene acetate was not found in the plants with which the present paper is concerned.

† The examination of herbarium specimens and colour slides was undertaken by Dr. E. E. Sherff (*cf.* ref. 4), for whose expert advice we are most grateful.

<sup>1</sup> Part XLVIII, M. R. Ord, C. M. Pigginn, and V. Thaller, *J.C.S. Perkin I*, 1975, 687.

<sup>2</sup> More detailed accounts of parts of the work described in this paper are in the D.Phil. Theses of (a) D. Bhattacharjee, Oxford, 1968; (b) J. R. F. Fairbrother, Oxford, 1965; and (c) S. Safe, Oxford, 1965.

Taxonomical inspection of the plants considered<sup>3</sup> to be *Dahlia merckii* revealed them to consist mainly of *Dahlia scapigera* (A. Dietr.) Link and Otto var. *scapigera* f. *scapigera* admixed with a few specimens of *Dahlia scapigera* var. *scapigera* f. *merckii* (Lehm.) Sherff.† The polyacetylene content of the latter species was analysed by Kaufmann and Lam,<sup>5</sup> and, as *Dahlia merckii* (Lehm.) by Bohlmann and Kleine;<sup>6</sup> it was therefore not re-investigated.

In the roots of f. *scapigera* the C<sub>14</sub> ene-diyne-diene acetate (XXVII) and the corresponding alcohol (XXVI) were the major polyacetylenic constituents (*cf.* f. *merckii*<sup>6</sup>); traces of several others were also present and some were identified.

The new, crystalline, and very unstable C<sub>16</sub> ene-diyne-diene alcohol (XXXII) was the main polyacetylene in the

<sup>3</sup> Sir Ewart R. H. Jones, *Chem. in Britain*, 1966, 2, 6.

<sup>4</sup> C. Chin, M. C. Cutler, Sir Ewart R. H. Jones, J. Lee, S. Safe, and V. Thaller, *J. Chem. Soc. (C)*, 1970, 314.

<sup>5</sup> F. Kaufmann and J. Lam, *Acta Chem. Scand.*, 1965, 19, 1267.

<sup>6</sup> F. Bohlmann and K.-M. Kleine, *Chem. Ber.*, 1965, 98, 872.

Polyacetylenes from *D. scapigera* and Dahlia hybrids

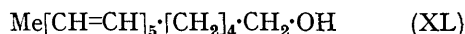
		Concn.*	Plant	Ref.
	<b>C<sub>13</sub></b>			
(I)	Me[C≡C] <sub>5</sub> ·CH=CH <sub>2</sub>	s	C	a
(II)	Me[C≡C] <sub>4</sub> ·[CH=CH] <sub>2</sub> H	s	C	14
(III)	Me[C≡C] <sub>3</sub> ·[CH=CH] <sub>3</sub> H	s-m	BC	b
(IV)	Me[C≡C] <sub>3</sub> Ph	s-l	BCG	cf. 4 †
(V)	MeCH=CH·[C≡C] <sub>2</sub> ·CH=CH <sub>2</sub>	s	ABCDH	cf. 4
(VI)	MeCH=CH·[C≡C] <sub>2</sub> ·CH=CH <sub>2</sub>	s	C	c
(VII)	HO·CH <sub>2</sub> ·CH=CH·[C≡C] <sub>4</sub> ·CH=CH <sub>2</sub>	s	B	cf. 4
(VIII)	AcO·CH <sub>2</sub> ·CH=CH·[C≡C] <sub>4</sub> ·CH=CH <sub>2</sub>	m	B	cf. 4
(IX)	MeCH=CH·[C≡C] <sub>3</sub> ·[CH=CH] <sub>2</sub> H	s	ABCDEFGH	cf. 4
(X)	HO·CH <sub>2</sub> ·CH=CH·[C≡C] <sub>3</sub> ·[CH=CH] <sub>2</sub> H	s	BCDEFGH	cf. 4
(XI)	AcO·CH <sub>2</sub> ·CH=CH·[C≡C] <sub>3</sub> ·[CH=CH] <sub>2</sub> H	s-m	BCDH	cf. 4
(XII)	MeCH=CH·[C≡C] <sub>2</sub> ·[CH=CH] <sub>3</sub> H	s-m	ABCE	d
(XIII)	HO·CH <sub>2</sub> ·CH=CH·[C≡C] <sub>2</sub> ·[CH=CH] <sub>3</sub> H	s	E	e
(XIV)	AcO·CH <sub>2</sub> ·CH=CH·[C≡C] <sub>2</sub> ·[CH=CH] <sub>3</sub> H	m	B	e
(XV)	MeCH=CH·[C≡C] <sub>2</sub> Ph	m-l	BCDFGH	cf. 4
(XVI)	HO·CH <sub>2</sub> ·CH=CH·[C≡C] <sub>2</sub> Ph	s-m	FG	f
(XVII)	AcO·CH <sub>2</sub> ·CH=CH·[C≡C] <sub>2</sub> Ph	m	B	f
(XVIII)	MeCH=CH·[C≡C] <sub>2</sub> ·CH=CH·CH(OH)·CH(OH)·CH=CH <sub>2</sub>	s	B	
(XIX)	MeCH=CH·[C≡C] <sub>2</sub> ·CH=CH·CH(OAc)·CH(OAc)·CH=CH <sub>2</sub>	m	B	
	<b>C<sub>14</sub></b>			
(XX)	Me[C≡C] <sub>3</sub> ·[CH=CH] <sub>2</sub> ·[CH <sub>2</sub> ] <sub>2</sub> ·CH <sub>2</sub> ·OH	s	B	cf. 4
(XXI)	Me[C≡C] <sub>3</sub> ·[CH=CH] <sub>2</sub> ·[CH <sub>2</sub> ] <sub>2</sub> ·CH <sub>2</sub> ·OAc	s-m	BC	cf. 4
(XXII)	Me[C≡C] <sub>3</sub> ·[CH=CH] <sub>2</sub> ·CH(OH)·CH <sub>2</sub> ·CH <sub>2</sub> ·OH	s	BC	g
(XXIII)	Me[C≡C] <sub>3</sub> ·[CH=CH] <sub>2</sub> ·CH(OAc)·CH <sub>2</sub> ·CH <sub>2</sub> ·OAc	s-m	BC	cf. 4
(XXIV)	Me[C≡C] <sub>3</sub> ·CH=CH·CH·CH(OH)·CH <sub>2</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> ·O	l	D	4
(XXV)	Me[C≡C] <sub>3</sub> ·CH=CH·CH·CH(OAc)·CH <sub>2</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> ·O	m-l	DGH	4
(XXVI)	MeCH=CH·[C≡C] <sub>2</sub> ·[CH=CH] <sub>2</sub> ·[CH <sub>2</sub> ] <sub>2</sub> ·CH <sub>2</sub> ·OH	s-l	AEH	6
(XXVII)	MeCH=CH·[C≡C] <sub>2</sub> ·[CH=CH] <sub>2</sub> ·[CH <sub>2</sub> ] <sub>2</sub> ·CH <sub>2</sub> ·OAc	s-l	ABEFH	6
(XXVIII)	MeCH=CH·[C≡C] <sub>2</sub> ·[CH=CH] <sub>2</sub> ·CH(OH)·CH <sub>2</sub> ·CH <sub>2</sub> ·OH	s-m	BDFGH	
(XXIX)	MeCH=CH·[C≡C] <sub>2</sub> ·[CH=CH] <sub>2</sub> ·CH(OAc)·CH <sub>2</sub> ·CH <sub>2</sub> ·OAc	s-l	BCDEFGH	
(XXX)	MeCH=CH·[C≡C] <sub>2</sub> ·CH=CH·CH·CH(OH)·CH <sub>2</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> ·O	m	F	4
(XXXI)	MeCH=CH·[C≡C] <sub>2</sub> ·CH=CH·CH·CH(OAc)·CH <sub>2</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> ·O	m	F	4
	<b>C<sub>16</sub></b>			
(XXXII)	MeCH=CH·[C≡C] <sub>2</sub> ·[CH=CH] <sub>2</sub> ·[CH <sub>2</sub> ] <sub>4</sub> ·CH <sub>2</sub> ·OH	m	A	
(XXXIII)	MeCH=CH·[C≡C] <sub>2</sub> ·[CH=CH] <sub>2</sub> ·[CH <sub>2</sub> ] <sub>4</sub> ·CH <sub>2</sub> ·OAc	s	A	
(XXXIV)	Me[CH=CH] <sub>2</sub> ·C≡C·CH <sub>2</sub> ·CH=CH·[CH <sub>2</sub> ] <sub>5</sub> ·CH <sub>2</sub> ·OH	s	A	6
	<b>C<sub>17</sub></b>			
(XXXV)	Me[C≡C] <sub>3</sub> ·[CH=CH] <sub>2</sub> ·[CH <sub>2</sub> ] <sub>4</sub> ·CH=CH <sub>2</sub>	s-m	BCDG	cf. 4
(XXXVI)	Me[C≡C] <sub>3</sub> ·[CH=CH] <sub>2</sub> ·CH(OH)·[CH <sub>2</sub> ] <sub>3</sub> ·CH=CH <sub>2</sub>	s	D	
(XXXVII)	Me[C≡C] <sub>3</sub> ·[CH=CH] <sub>2</sub> ·CH(OAc)·[CH <sub>2</sub> ] <sub>3</sub> ·CH=CH <sub>2</sub>	s	DG	
(XXXVIII)	Me[C≡C] <sub>3</sub> ·CH=CH·[CH <sub>2</sub> ] <sub>6</sub> ·CH=CH <sub>2</sub>	s	C	h
(XXXIX)	MeCH=CH·[C≡C] <sub>2</sub> ·[CH=CH] <sub>2</sub> ·[CH <sub>2</sub> ] <sub>4</sub> ·CH=CH <sub>2</sub>	s	F	cf. 4

\* l, > 500 mg; m, 50—500 mg; s, < 50 mg polyacetylene per kg dried material. A, *Dahlia scapigera* var. *scapigera* f. *scapigera*; B, Deerplay; C, Preference; D, Glorie van Heemstede; E, Gerrie Hoek; F, Roulette; G, Dolce vita; H, Flocon de neige. † References cited in the earlier paper on Dahlias (ref. 4) are not repeated here.

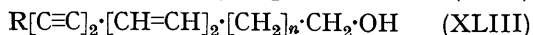
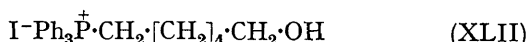
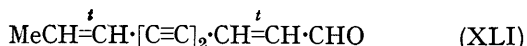
° J. S. Sørensen, D. Holme, E. T. Borland, and N. A. Sørensen, *Acta Chem. Scand.*, 1954, **8**, 1769. <sup>b</sup> F. Bohlmann, C. Arndt, H. Bornowski, H. Jastrow, and K. M. Kleine, *Chem. Ber.*, 1962, **95**, 1320. ° E. R. H. Jones, L. Skattebøl, and M. C. Whiting, *J. Chem. Soc.*, 1958, 1054. <sup>d</sup> J. S. Sørensen and N. A. Sørensen, *Acta Chem. Scand.*, 1954, **8**, 1741. ° F. Bohlmann, H. Bornowski, and S. Köhn, *Chem. Ber.*, 1964, **97**, 2583. <sup>f</sup> J. S. Sørensen and N. A. Sørensen, *Acta Chem. Scand.*, 1958, **12**, 756. ° F. Bohlmann and K. M. Kleine, *Chem. Ber.*, 1964, **97**, 1193. <sup>h</sup> F. Bohlmann, C. Arndt, and H. Bornowski, *Chem. Ber.*, 1960, **93**, 1937.

extract from dried leaves and flowers. Its structure followed unequivocally from spectral data and was confirmed by synthesis (see below). The  $C_{14}$  alcohol (XXVI) was also present in the leaves, being detected in the mother liquor from the crystallisation of the alcohol (XXXII). The  $C_{16}$  alcohol (XXXIV), one of the polyacetylenes with skipped unsaturation found in *f. merckii*,<sup>6</sup> was also detected in *f. scapigera*, but only in the extracts from fresh leaves. It was completely isomerised into the pentaen-ol (XL) with methanolic potash (4%) at 50 °C.

The differences observed between the extracts from fresh upper parts [presence of the alcohol (XXXIV) and *ca.* twice the amount of the alcohol (XXXII)] and dried ones could be due either to the different stage of growth at which the leaves happened to be harvested (beginning of flowering for the fresh greenery, end of the flowering period for the material to be dried) or, more likely, to the destruction of the compounds by the drying process itself (several weeks at 20–25 °C). Analogous drying appeared to have little effect on the polyacetylene content of *D. coccinea*.<sup>4</sup> No ether-soluble polyacetylenic artefacts were produced in either case.



The  $C_{16}$  alcohol (XXXII) was synthesised from matricarinal (XLI) and the phosphorane prepared from the crystalline phosphonium iodide (XLII) (the corresponding tetrahydropyranil Wittig salt could not be induced to crystallise); a sufficient amount of butyllithium (1.9 mol. equiv.) was used to convert the alcohol into the alkoxide (hydroxyphosphoranes had been used in Wittig reactions before<sup>7</sup>). The crude alcohol (XXXII) was a mixture of *trans,cis*- and *trans,trans*-isomers in which the latter predominated; the yield was not high (16%), but the method was shown in exploratory experiments<sup>2a</sup> to be generally applicable to the synthesis of the homologous alcohols (XLIII;  $n = 0, 1, 4-6$ ;  $\text{R} = \text{MeCH}=\text{CH}, \text{MeC}\equiv\text{C}, \text{ or Ph}$ ).



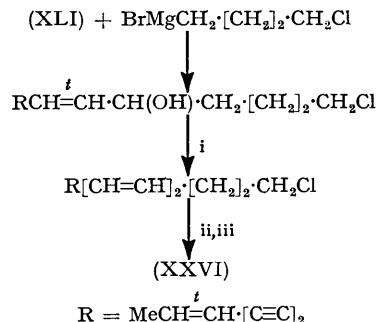
The  $C_{14}$  alcohol (XXVI) was synthesised by the reactions of Scheme 1, again in moderate overall yield (12%). This is seemingly more convenient than the method described<sup>8</sup> and was shown<sup>2a</sup> to be suitable also for the preparation of the higher members of the same homologous series (XLIII;  $n = 2-6$ ).

Although modest in size, the genus *Dahlia* has given rise to a large number of horticultural varieties. These have been classified by horticulturalists into groups according to the shape of their flowers and height of growth.<sup>9</sup> Representatives of the following horticultural groups have been analysed for their polyacetylene con-

<sup>7</sup> Cf. I. T. Harrison and B. Lythgoe, *J. Chem. Soc.*, 1958, 843.

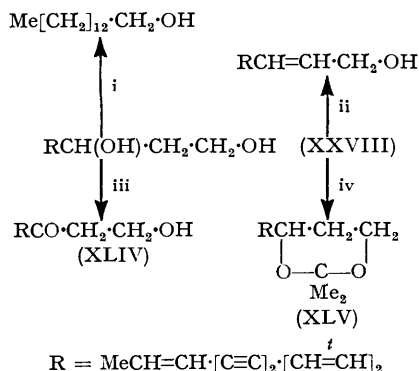
<sup>8</sup> F. Bohlmann, B. Diedrich, W. Gordon, I. Faughänel, and J. Schneider, *Tetrahedron Letters*, 1965, 1385.

tent: Cactus (Deerplay and Preference), Decorative (Glorie van Heemstede and Gerrie Hock), Anemone-flowered (Roulette), and Colibri Dahlias (Dolce vita and Flocon de neige).



SCHEME 1 Reagents: i, *p*-MeC<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H·C<sub>6</sub>H<sub>6</sub> (80 °C); ii, anhydr. KOAc-HCO-NMe<sub>2</sub> (100–110 °C); iii, KOH-MeOH (4%) (20 °C)

Six new polyacetylenes have been isolated from the hybrids examined, and Deerplay contained four of them: the  $C_{13}$  diol (XVIII) and diacetate (XIX) and the  $C_{14}$  diol (XXVIII) and diacetate (XXIX). All were crystalline and the alcohol-acetate relationships were established through hydrolysis of the more abundant acetates. For the  $C_{13}$  compounds integration of the ethylenic proton signals and those of protons on carbon carrying oxygen in the n.m.r. spectrum, hydrogen uptake on microhydrogenation, and i.r. bands established the presence of a vinyl group separated from the ene-diyne-ene chromophore by a glycol group. This was confirmed by a bathochromic u.v. shift of 25 nm on treatment of the diol (XVIII) with periodate, and the formation from the periodate cleavage product of decan-1-ol on hydrogenation and reduction with sodium borohydride. No i.r. band around 800 cm<sup>-1</sup> was observed and therefore the presence of *trans*-double bonds only was indicated.



SCHEME 2 Reagents: i, H<sub>2</sub>, Pt, EtOH-HCl; ii, HCl-EtOH; iii, MnO<sub>2</sub>; iv, Me<sub>2</sub>CO-*p*-MeC<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H

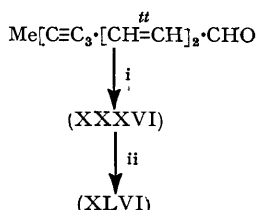
The properties of the  $C_{14}$  diol (XXVIII) and its *trans*-formation products (Scheme 2) established the structures of these new  $C_{14}$  compounds. The failure of the diol to react with periodate and its conversion into the hydroxyketone (XLIV) (clear n.m.r. signals for CO·CH<sub>2</sub>·CH<sub>2</sub>·OH)

<sup>9</sup> In Great Britain, The National Dahlia Society issues Classified Lists of Dahlias; the 10th edition was published in 1966

and the dioxolan (XLV) proved the presence of a 1,3-diol. The chromophore orientation was deduced from the u.v. spectrum of the product obtained by treatment of the diol with acid: this was similar to the ene-diyne-triene absorption of the  $C_{13}$  hydrocarbon (XII) and alcohol (XIII) and differed from the alternative diene-diyne-diene absorption<sup>10</sup> below 300 nm. The absence of i.r. bands around  $800\text{ cm}^{-1}$  indicated the presence of *trans*-double bonds.

The new  $C_{17}$  alcohol (XXXVI) and its acetate (XXXVII) were both isolated from the hybrid Glorie van Heemstede; only the acetate was obtained from *Dolce vita*. The alcohol gave heptadecan-6-ol on hydrogenation and the ketone (XLVI) on oxidation with manganese dioxide. I.r. bands ( $3080$  and  $920\text{ cm}^{-1}$ ) indicated the presence of a vinyl group in addition to the triyne-diene unsaturation. The racemic alcohol (XXXVI) and the ketone (XLVI) were readily synthesised (Scheme 3).

The Table shows that some polyacetylenes occur only sporadically, whereas others are present in several of the Dahlias examined; only one polyacetylene, the  $C_{13}$  hydrocarbon (IX), was detected in all of them in trace amounts. The polyacetylene concentration in the leaves changed considerably during the growing season<sup>2c</sup> but



SCHEME 3 Reagents: i,  $\text{BrMgCH}_2\cdot[\text{CH}_2]_2\cdot\text{CH}=\text{CH}_2$ ; ii,  $\text{MnO}_2$

the range of polyacetylenes present appeared to be unchanged. The polyacetylene concentration (mg per kg) was at a minimum during the early stages of growth and at a maximum 2–3 weeks after flowering had begun; it decreased during the later part of the season. When more than one polyacetylene occurred in the leaves, the seasonal changes in concentration of the main components were similar [e.g. in the hybrid *Preference*, the  $C_{17}$  hydrocarbon (XXXV) and  $C_{13}$  hydrocarbon (III)]. Of the one species (*D. coccinea*<sup>4</sup>) and seven hybrids examined, only one, *Flocon de neige*, contained no polyacetylenes in the leaves over the whole period examined, but the tetrahydropyranyl acetate (XXV) appeared in the flowers.

Polyacetylenes were also detected after 2–3 days in *Dahlia* seedlings grown in the dark. Only an ene-tetraene chromophore was well defined; the maximum concentration was reached after 6–7 days. An ester group indicated by the i.r. spectrum and t.l.c. behaviour pointed to the presence of the  $C_{13}$  acetate (VIII); this was encountered in only one of the fully grown plants examined.

#### EXPERIMENTAL

The general techniques and procedures for the isolation of polyacetylenes from roots, leaves, and flowers and the

estimation of the concentration of known polyacetylenes are those described in Part XXXI<sup>4</sup> unless stated otherwise.

*D. scapigera*.—*Roots*. The tubers (1.37 kg; equiv. dry weight 0.275 kg) contained the hydrocarbons (V) (25 mg), (IX) (1 mg), and (XII) (5 mg) (an apparent ene-tetraene could not be identified), the  $C_{14}$  acetate (XXVII) (1.22 g) (the mother liquor contained traces of compounds with ene-tetraene, ene-tetraene, ene-triene-diene, and diene-diene chromophores), and the  $C_{14}$  alcohol (XXVI) (100 mg), again accompanied by traces of compounds with ene-tetraene, ene-tetraene, and ene-triene-diene chromophores. The most polar polyacetylene, possibly a diol, with  $\lambda_{\text{max}}$  313, 292, and 273 nm (traces), could not be identified.

*Leaves*. (a) The dried leaves (2.17 kg) contained only cosmene (2,6-dimethylocta-1,3,5,7-tetraene) (*ca.* 400 mg) and a mixture of at least three (3 spots on 5%  $\text{AgNO}_3\text{-SiO}_2$  plates)  $C_{20}$  trienes (*ca.* 300 mg) [ $M^+$  268 ( $C_{20}H_{28}$ )],  $\lambda_{\text{max}}$  283, 272, and 263 nm, in the hydrocarbon fraction, the  $C_{16}$  acetate (XXXIII) (*ca.* 20 mg) [isolated only as the alcohol (XXXII) on treatment (12 h at  $20^\circ\text{C}$ ) of the carotene-containing acetate fraction with  $\text{KOH-MeOH}$  (4%)], and an alcohol fraction heavily contaminated with chlorophyll. This fraction was treated with  $\text{KOH}$  as above and gave on chromatography and crystallisation ( $\text{CH}_2\text{Cl}_2\text{-petrol}$ ) *hexadeca-6,8,14-triene-10,12-diyne-1-ol* (XXXII) (120 mg), m.p.  $85\text{--}87^\circ$  (Found: C, 83.7; H, 8.8.  $C_{16}H_{20}O$  requires C, 84.15; H, 8.85%),  $\lambda_{\text{max}}$  (MeOH) 337 ( $\epsilon$  28 000), 316 (38 200), 296 (28 500), 281 (16 800), 267 (27 500), and 252 nm (32 000),  $\nu_{\text{max}}$  ( $\text{CHCl}_3$ ) 3 600 and 3 400 ( $\text{OH}$ ), 2 190 and 2 120 ( $\text{C}\equiv\text{C}$ ), 980 (*trans,trans-CH=CH\cdot CH=CH*), and  $945\text{ cm}^{-1}$  (*trans-CH=CH*),  $\nu_{\text{max}}$  ( $\text{CS}_2$ ) 980 and  $945\text{ cm}^{-1}$ ,  $\tau$  ( $\text{CDCl}_3$ ) 8—8.7 (6 H, m,  $[\text{CH}_2]_3\cdot\text{CH}_2\cdot\text{O}$ ), 8.35 (1 H, s, OH), 8.16 (3 H, dd,  $J$  7 and 1.5 Hz,  $\text{CH}_3\cdot\text{CH}=\text{CH}$ ), 7.83 (2 H, m,  $=\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2$ ), 6.35 (2 H, t,  $J$  6 Hz,  $\text{CH}_2\cdot\text{OH}$ ), and 3.05—4.5 (6 H, m,  $\text{CH}=\text{CH}$  and  $\text{HC}=\text{CH}=\text{CH}$ ), *m/e* 228 ( $M^+$ , 75%) and 141 (100); a sample of the mother liquor from the above crystallisation (*m/e* 228, 200, and 141) gave on hydrogenation (Pd-C) *hexadecan-1-ol* and *tetradecan-1-ol* (identified by comparative g.l.c. with authentic specimens) thus proving the presence of the  $C_{14}$  alcohol (XXVI) (30 mg).

(b) The polyacetylenes of the fresh upper parts of the plant were not isolated; their approximate concentrations were estimated from the u.v. spectra and the known  $\epsilon$  values). Fresh leaves and stems (2.5 kg; equiv. to *ca.* 0.375 kg dry weight), picked at the start of flowering, were extracted with  $\text{Me}_2\text{CO}$  and the extract was transferred into  $\text{Et}_2\text{O}$ . The gum obtained on concentration of the  $\text{Et}_2\text{O}$  solution was triturated with  $\text{petrol-Et}_2\text{O}$  (9:1) and the extract was separated by gradient elution chromatography [ $\text{SiO}_2$ ;  $\text{petrol-Et}_2\text{O}$  (9:1) to  $\text{Et}_2\text{O}$ ]. Cosmene and the  $C_{20}$  trienes appeared together (*ca.* 50 mg) and were not separated. Traces of an ene-diyne-diene acetate were followed by the  $C_{16}$  dienyne alcohol (XXXIV) (*ca.* 50 mg) and a mixture of the  $C_{16}$  alcohols (XXXIV) and (XXXII) and the  $C_{14}$  alcohol (XXVI) contaminated with chlorophyll. This mixture was treated with  $\text{KOH-MeOH}$  (4%) for 24 h at  $24^\circ\text{C}$ ; chromatography [ $\text{petrol-Et}_2\text{O}$  (4:1) to  $\text{Et}_2\text{O}$ ] gave unchanged alcohol (XXXIV) (*ca.* 50 mg), *hexadecapentaenol* (XL) (*ca.* 50 mg), and a mixture of the  $C_{14}$  alcohol (XXVI) and the  $C_{16}$  alcohol (XXXII) (*ca.* 50 mg). With  $\text{KOH-MeOH}$  (4%) for 5 h at  $50^\circ\text{C}$  (XXXIV) was completely isomerised to the pentaenol (XL).

*Flowers*. The dried and milled flowers (105 g) showed a

<sup>10</sup> F. Bohlmann and H. G. Viehe, *Chem. Ber.*, 1955, **88**, 1245.

very similar polyacetylene composition to that of the dried leaves.

**Synthesis of all-trans-Hexadeca-6,8,14-triene-10,12-diyn-1-ol (XXXII).**—Bu<sup>n</sup>Li in hexane (0.4M; 7 ml, 2.8 mmol) was added to the phosphonium salt (XLI) <sup>11</sup> (735 mg, 1.5 mmol) stirred in Et<sub>2</sub>O (30 ml) at 20 °C under N<sub>2</sub>. After 0.5 h the aldehyde (XLI) <sup>12</sup> (144 mg, 1 mmol) was added dropwise to the orange-coloured suspension and the resulting cream-coloured mixture was stirred for 0.5 h before H<sub>2</sub>O (10 ml) was added. The Et<sub>2</sub>O extract was chromatographed repeatedly on SiO<sub>2</sub> columns and gave a mixture of *cis,trans*- and *trans,trans*-isomers (36 mg, 16%) which was crystallised (Et<sub>2</sub>O-petrol) and gave the all-*trans*-alcohol (XXXII), m.p. and mixed m.p. 87–88 and 85–88°, respectively; the spectra were identical to those recorded for the natural product.

**Synthesis of all-trans-Tetradeca-4,6-12-triene-8,10-diyn-1-ol (XXVI).**—The aldehyde (XLI) (430 mg, 3 mmol) and the Grignard reagent from Mg turnings (720 mg, 30 mmol) and 1-bromo-4-chlorobutane <sup>13</sup> (5.2 g, 30 mmol) in Et<sub>2</sub>O (70 ml) were allowed to react for 0.5 h. Work-up and chromatography of the Et<sub>2</sub>O extract gave a fraction containing the ene-diyn-ene chloro-alcohol (ca. 300 mg). This and *p*-MeC<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H (500 mg) were refluxed in C<sub>6</sub>H<sub>6</sub> (20 ml) for 0.5 h. Work-up and chromatography gave two ene-diene fractions; the more polar one and anhydrous KOAc (1 g) were stirred in HCO·NMe<sub>2</sub> (10 ml) at 100–110 °C for 1 h. Transfer into Et<sub>2</sub>O and chromatography of the concentrated Et<sub>2</sub>O extract yielded an ene-diene diene acetate fraction. This was kept in KOH-MeOH (4%; 15 ml) for 12 h at 20 °C; the product was transferred into Et<sub>2</sub>O and chromatographed, and the alcohol fraction was crystallised (Et<sub>2</sub>O-petrol) yielding the alcohol (XXVI) (75 mg, 12%), m.p. 111° (lit.,<sup>6</sup> 110–111°) (Found: C, 83.6; H, 7.7. Calc. for C<sub>14</sub>H<sub>16</sub>O: C, 84.0; H, 8.0%), λ<sub>max</sub> (MeOH) 337 (ε 28 700), 316 (39 000), 296 (29 000), 281 (16 000), 267 (28 500), and 252 nm (31 800), ν<sub>max</sub> (CS<sub>2</sub>) 980 and 947 cm<sup>-1</sup>.

**Deerplay (Tall, Cactus-flowered, Yellow).**—**Roots.** The tubers (7 kg; equiv. dry weight 1.4 kg) contained the hydrocarbons (V) (14 mg), (IX) (14 mg), (XV) (8 g), (IV) (10 mg), and (XII) (10 mg), the acetates (XVII) (280 mg), (VIII) (ca. 35 mg), (XI) (ca. 70 mg), (XXVII) (30 mg), (XIV) (ca. 3 mg), 3,4-diacetoxytrideca-1,trans-5,trans-11-triene-7,9-diyn-1-ol (XIX) (280 mg), m.p. 52–53° (from petrol at -40 °C) [Found: C, 71.0; H, 6.55%; M (osmometer), 285. C<sub>17</sub>H<sub>18</sub>O requires C, 71.3; H, 6.35%; M, 286], [α]<sub>D</sub><sup>23</sup> +147° (c. 1.010 in EtOH), λ<sub>max</sub> (EtOH) 313 (ε 18 000), 293 (21 500), 277 (14 500), 262 (8 000), 247.5 (22 500), 238 (31 000), and 230 nm (31 000), ν<sub>max</sub> (CCl<sub>4</sub>) 3 090, 1 430, 987, and 915 (infl.) (CH=CH<sub>2</sub>), 3 016, 950, 945 (infl.), and 935 (infl.) (*trans*-CH=CH), 2 210 (C=C), 1 755 (C=O), and 1 240, 1 220, and 1 025 cm<sup>-1</sup> (O-CO), no ν<sub>max</sub> (CS<sub>2</sub>) around 800 cm<sup>-1</sup>, τ (CCl<sub>4</sub>) 8.16 (3 H, dd, J 7 and 1.5 Hz, CH<sub>3</sub>·CH=CH), 7.90 (6 H, s, OAc), ca. 4.8 (2 H, m, CHOAc), and 3.2–4.9 (7 H, m, CH=CH and CH=CH<sub>2</sub>), and 1,3-diacetoxytetradeca-trans-4,trans-6,trans-12-triene-8,10-diyn-1-ol (XXIX) (200 mg), m.p. 35–36° (from Et<sub>2</sub>O-petrol and CHCl<sub>3</sub>-petrol) [Found: C, 72.05; H, 6.7%; M, 301.5 (osmometer). C<sub>18</sub>H<sub>20</sub>O<sub>4</sub> requires C, 72.0; H, 6.7%; M, 300], [α]<sub>D</sub><sup>24</sup> +89° (c. 1.250 in EtOH), λ<sub>max</sub> (EtOH) 336 (ε 30 500), 314.5 (40 500), 296 (29 200), 279 (16 500), 266 (30 000), and 247 nm (34 500), ν<sub>max</sub> (CCl<sub>4</sub>) 2 205 (C=C), 1 755 (C=O), 1 235, 1 045, and 1 025 (O-CO), and 979 and 953 cm<sup>-1</sup> (*trans* CH=CH·CH=CH and CH=CH), no ν<sub>max</sub> (CS<sub>2</sub>)

<sup>11</sup> A. R. Hands and A. J. H. Mercer, *J. Chem. Soc. (C)*, 1968, 1331.

around 800 cm<sup>-1</sup>, τ (CDCl<sub>3</sub>) 8.16 (3 H, dd, J 7 and 1.5 Hz, CH<sub>3</sub>·CH=CH), ca. 8 (2 H, m, O·CH·CH<sub>2</sub>·CH<sub>2</sub>·O), 7.95 and 7.93 (each 3 H, s, OAc), 5.87 (2 H, t, J 6.5 Hz, CH<sub>2</sub>·CH<sub>2</sub>·O), 4.5 (1 H, m, =CH·CH·O), and 3.0–4.7 (6 H, m, CH=CH), and small amounts (less than 50 mg of each) of the alcohols (VII), (X), (XVIII), and (XXVIII).

**Flowers.** The dried flowers (1.7 kg) contained the hydrocarbons (XXXV) (340 mg), (IV) (8 mg), and (III) (8 mg), the acetates (XXI) (170 mg) and (XXIII) (50 mg), and the alcohol (XX) (30 mg).

**Leaves.** The dried leaves (1 kg) contained only traces of the hydrocarbon (XXXV) and of the alcohol (XX).

**Transformations of the C<sub>13</sub> Diacetate (XIX).**—This (50 mg) was kept with NaOH-MeOH (4%; 10 ml) for 1 h at 20 °C and gave on work-up *trideca*-1,trans-5,trans-11-triene-7,9-diyn-3,4-diol (XVIII) (32 mg), plates (from CH<sub>2</sub>Cl<sub>2</sub>-petrol), m.p. 83–84° (Found: C, 76.1; H, 7.3. C<sub>13</sub>H<sub>14</sub>O<sub>2</sub> requires C, 77.2; H, 7.0%), [α]<sub>D</sub><sup>25</sup> +28° (c. 0.640 in EtOH), λ<sub>max</sub> (EtOH) 312 (ε 18 700), 293 (23 300), 277 (15 700), 261 (8 300), 248 21 500), 237 (29 500), and 230 nm (29 500), ν<sub>max</sub> (CHCl<sub>3</sub>) 3 560, 3 390, and 1 120–1 085 (OH), 3 080 and 1 425 (CH=CH<sub>2</sub>), 2 205 and 2 177 (C=C), and 1 627 and 947 cm<sup>-1</sup> (*trans*-CH=CH), τ (CDCl<sub>3</sub>) 8.15 (3 H, dd, J 7.2 and 1.5 Hz, CH<sub>3</sub>·CH=CH), 7.55br (2 H, m, OH), 5.73 (2 H, m, CH·OH), and 3.45–4.83 (7 H, m, CH=CH and CH=CH<sub>2</sub>).

The diol (XVIII) (5.31 mg) was hydrogenated in a Hösli microhydrogenator over Pd in EtOH and took up 4.82 ml of H<sub>2</sub> (21 °C; 764 mmHg) corresponding to 7.2 mol. equiv.

The diol (XVIII) (5 mg) in Et<sub>2</sub>O (10 ml) and NaIO<sub>4</sub> (20 mg) in H<sub>2</sub>O (10 ml) were shaken for 20 h. The Et<sub>2</sub>O solution had λ<sub>max</sub> 337.5 (rel. E 1.0), 317.5 (1.2), 297.5 (0.95), 257.5 (0.65), 261 (1.4), and 248 nm (1.6). It was concentrated and the residue was first hydrogenated (5% Pd-C) in EtOH, and then treated with NaBH<sub>4</sub> in MeOH. The product and decan-1-ol had identical t<sub>R</sub> values (12.8 min at 120 °C).

**Transformations of the C<sub>14</sub> Diacetate (XXIX).**—This (600 mg) was kept with NaOH-MeOH (4%; 20 ml) for 1 h at 20 °C and gave, on work-up, needles (from CH<sub>2</sub>Cl<sub>2</sub>-petrol) of *tetradeca*-trans-4,trans-6,trans-12-triene-8,10-diyn-1,3-diol (XXVIII) (350 mg), m.p. 96–97° [Found: C, 77.6; H, 7.65%; M, 214 (osmometer). C<sub>14</sub>H<sub>16</sub>O<sub>2</sub> requires C, 77.75; H, 7.45%; M, 216], [α]<sub>D</sub><sup>20</sup> -19° (c. 1.100 in EtOH), λ<sub>max</sub> (EtOH) 336 (ε 29 600), 314.5 (40 800), 296 (30 000), 279 (16 800), 266 (29 400), and 250 nm (33 300), ν<sub>max</sub> (CHCl<sub>3</sub>) 2 200 and 2 130 (C=C), 1 100 and 1 055 (CHOH), 987 (*trans,trans*-CH=CH·CH=CH), and 950 cm<sup>-1</sup> (*trans*-CH=CH), τ (CDCl<sub>3</sub>) 8.2 (2 H, m, O·CH·CH<sub>2</sub>·CH<sub>2</sub>·O), 8.17 (3 H, dd, J 7 and 1.5 Hz, CH<sub>3</sub>·CH=CH), 6.84 (2 H, s, OH), 6.17 (2 H, t, J 5.5 Hz, CH<sub>2</sub>·CH<sub>2</sub>·O), 5.54 [1 H, dt, J 5.5 and 5.5 Hz, =CH·CH(O)·CH<sub>2</sub>], and 3.0–4.6 (6 H, m, CH=CH).

The diol (XXVIII) (50 mg) and MnO<sub>2</sub> (250 mg) in CH<sub>2</sub>Cl<sub>2</sub> (25 ml) were shaken for 2 h at 20 °C. Usual work-up, SiO<sub>2</sub> chromatography (petrol-Et<sub>2</sub>O, 1:1), and crystallisation (CH<sub>2</sub>Cl<sub>2</sub>-petrol) gave needles of *all-trans*-1-hydroxytetradeca-4,6,12-triene-8,10-diyn-3-one (XLIV) (29 mg), m.p. 103–104° λ<sub>max</sub> (EtOH) 359infl. (ε 26 500), 339 (35 500), 322infl. (29 500), 303 (17 500), 274 (19 000), 263 (19 500), and 212 nm (20 000), ν<sub>max</sub> (CHCl<sub>3</sub>) 3 500br and 1 078 (OH and CH<sub>2</sub>OH), 2 193 (C=C), 1 660 and 1 593 (CH=CH·CO), 988 (*trans,trans*-CH=CH·CH=CH), and 948 cm<sup>-1</sup> (*trans*-CH=CH), τ (CDCl<sub>3</sub>)

<sup>12</sup> F. Bohlmann and H. J. Mannhardt, *Chem. Ber.*, 1955, **88**, 1330.

<sup>13</sup> D. Starr and R. M. Hixon, *J. Amer. Chem. Soc.*, 1934, **56**, 1595.

8.15 (3 H, dt,  $J$  7 and 1.5 Hz,  $\text{CH}_3\text{-CH=CH}$ ), 7.45br (1 H, s, OH), 7.17 (2 H, t,  $J$  5.5 Hz,  $\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}$ ), 6.07 (2 H, t,  $J$  5.5 Hz,  $\text{CH}_2\cdot\text{CH}_2\cdot\text{O}$ ), and 2.57—4.52 (6 H, m,  $\text{CH=CH}$ ).

The diol (XXVIII) (2.59 mg) was hydrogenated over Pd in EtOH in the Hösli microhydrogenator and took up 1.99 ml of  $\text{H}_2$  at 11 °C and 772 mmHg (7.0 mol. equiv.).

When it (10 mg) was hydrogenated over Pt (from 10 mg  $\text{PtO}_2$ ) in EtOH-HCl (conc.) (4 : 1; 10 ml), the main product and tetradecan-1-ol had identical  $t_R$  values (7.2 min at 188 °C).

The diol (100 mg) and  $p\text{-MeC}_6\text{H}_4\cdot\text{SO}_3\text{H}$  (50 mg) were kept in dry  $\text{Me}_2\text{CO}$  (50 ml) for 12 h at 20°. Work-up with  $\text{K}_2\text{CO}_3$ , chromatography, and crystallisation (from petrol at -40°) yielded 2,2-dimethyl-4-(all-trans-undeca-1,3,9-triene-5,7-diynyl)dioxolan (XLV) (56 mg), m.p. 76—77°,  $[\alpha]_D^{21} +19^\circ$  ( $c$  1.07 in EtOH),  $\lambda_{\text{max}}$  (EtOH) 335.5 ( $\epsilon$  36 500), 314 (49 500), 291 (36 000), 279 (20 200), 266 (35 500), 250 (40 500), and 232.5 nm (22 300),  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 2 195 and 2 127 ( $\text{C}\equiv\text{C}$ ), 1 383 and 1 372 ( $\text{CMe}_2$ ), 1 196, 1 156, 1 129, and 1 095 ( $-\text{COC}-$ ), and 948  $\text{cm}^{-1}$  ( $\text{trans-CH=CH}$ ),  $\tau$  ( $\text{CCl}_4$ ) 8.68 and 8.60 (3 H each, s,  $\text{CH}_3\cdot\text{C}\cdot\text{CH}_3$ ), 8.6 (2 H, m,  $\text{O}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}$ ), 6.1 (2 H, m,  $\text{CH}_2\text{O}$ ), 5.5 (1 H, m,  $=\text{CH}\cdot\text{CHO}$ ), and 3.06—4.55 (6 H, m,  $\text{CH=CH}$ ).

The diol (XXVIII) (41 mg) was kept for 48 h in EtOH (20 ml)-HCl (conc.; 10 ml) at 20 °C. Extraction with  $\text{Et}_2\text{O}$  and chromatography [ $\text{SiO}_2$  (10 g)] from petrol-Et<sub>2</sub>O (4 : 1) gave tetradeca-2,4,6,12-tetraene-8,10-diyn-1-ol (15 mg, 40%; estimated from the u.v. spectrum) which did not crystallise,  $\lambda_{\text{max}}$  (Et<sub>2</sub>O) 353 (rel.E 1.0), 334 (1.1), 315 (0.9), 289 (0.5), 275 (0.5), and 266 nm (0.7).

*Preference (Tall, Cactus-flowered, Purple-white).—Roots.* The tubers (2.4 kg) contained the  $\text{C}_{13}$  hydrocarbons (XII) (30 mg), (IX) (ca. 1 mg), (XV) (600 mg), (VI) (ca. 2 mg), (III) (80 mg), and (IV) (250 mg), the acetates (XI) (6 mg), (XXIX) (80 mg), and (XXIII) (80 mg), and the alcohol (X) (4 mg).

*Flowers.* The dried flowers (460 g) contained the hydrocarbons (XXXV) (45 mg), (II) (7 mg), and (III) (140 mg) (traces of pentayne and ene-tetrayn-ene hydrocarbons were also detected) and the acetate (XXIII) (95 mg).

*Leaves.* Fresh leaves (2.9 kg) contained the hydrocarbons (XXXV) (30 mg), (XXXVIII) (2 mg), and (III) (20 mg) and the diol (XXII) (3 mg).

*Glorie van Heemstede (Decorative, Yellow).—Roots.* The tubers (7 kg; equiv. dry wt. 1.4 kg) contained the  $\text{C}_{13}$  hydrocarbons (V) (15 mg), (IX) (9 mg), and (XV) (2 g), the  $\text{C}_{13}$  acetate (XI) (1 mg), the  $\text{C}_{14}$  diacetate (XXIX) (10 mg), the  $\text{C}_{13}$  alcohol (X) (80 mg), and the  $\text{C}_{14}$  diol (XXVIII) (45 mg).

*Leaves.* The dried leaves (2 kg) contained the  $\text{C}_{17}$  hydrocarbon (XXXV) (440 mg), the acetates (XXXVII) (25 mg) [this gave on treatment with KOH-MeOH (4%); 24 h at 20 °C] the crystalline alcohol (XXXVI) and (XXV) (740 mg), heptadeca-1,7,9-triene-11,13,15-triyn-6-ol (XXXVI) (20 mg), very unstable crystals (from Et<sub>2</sub>O-petrol), m.p. 46—47°,  $[\alpha]_D^{20} -9^\circ$  ( $c$  0.65 in  $\text{CHCl}_3$ ),  $\lambda_{\text{max}}$  (EtOH) 347.5 ( $\epsilon$  34 500), 325 (41 000), 305.5 (27 000), 288 (15 500), 269 (100 000), 258.5 (53 000), and 246.5 nm (24 500),  $\nu_{\text{max}}$  ( $\text{CHCl}_3$ ) 3 590 and 3 420 (OH), 2 210 ( $\text{C}\equiv\text{C}$ ), 3 080 and 920 ( $\text{CH=CH}_2$ ), and 1 640, 1 585, and 985  $\text{cm}^{-1}$  ( $\text{trans,trans-CH=CH}\cdot\text{CH=CH}$ ),  $\nu_{\text{max}}$  ( $\text{CS}_2$ ) 985 and 915  $\text{cm}^{-1}$ ,  $\tau$  ( $\text{CDCl}_3$ ) 8.2—8.5 (4 H, m,  $[\text{CH}_2]_2$ ), 8.33 (1 H, s, OH), 7.96 (3 H, s,  $\text{CH}_3\cdot\text{C}\equiv\text{C}$ ), 7.7—8.0 (2 H, m,  $\text{CH}_2\cdot\text{CH=CH}_2$ ), 5.8 (1 H, m,

$\text{CHOH}$ ), 4.7—5.1 (3 H, m,  $\text{CH=CH}_2$ ), and 2.9—4.5 (4 H, m,  $\text{CH=CH}\cdot\text{CH=CH}$ ), and the  $\text{C}_{14}$  alcohol (XXIV) (120 mg).

*Transformations of the  $\text{C}_{17}$  Alcohol (XXXVI).—*This (2 mg) was hydrogenated in EtOH over Rh-C (5%). The hydrogenation product and heptadecan-6-ol had identical  $t_R$  values (34.7 min at 178 °C).

The alcohol (XXXVI) (13 mg) and  $\text{MnO}_2$  (100 mg) in Et<sub>2</sub>O (10 ml) were shaken for 4 h at 20 °C. Work-up, chromatography ( $\text{Al}_2\text{O}_3$ ), and crystallisation (petrol) gave unstable needles (7 mg) of heptadec-1,7,9-triene-11,13,15-triyn-6-one (XLVI), m.p. 107—108°, mixed m.p. 106—108°, spectra identical with those of the synthetic compound. The ketone (2 mg) was hydrogenated in EtOH over Rh-C (5%). The perhydro-ketone and heptadecan-6-one had identical  $t_R$  values (23.4 min at 181 °C).

*Synthesis of all-trans-Heptadeca-1,7,9-triene-11,13,15-triyn-6-ol (XXXVI).—*Dodeca-trans-2,trans-4-diene-6,8,10-triynal<sup>14</sup> (160 mg) in tetrahydrofuran (80 ml) was added to the stirred Grignard reagent prepared from 1-bromopent-4-ene<sup>15</sup> (140 mg) and Mg turnings (124 mg) in tetrahydrofuran (25 ml), under  $\text{N}_2$  at 20 °C over 20 min. After 10 min additional stirring, usual work-up, and chromatography ( $\text{SiO}_2$ ), the triyne-diene fraction yielded on crystallisation (petrol at -40 °C) unstable plates of the racemic alcohol (XXXVI) (40 mg), m.p. 45—46°, mixed m.p. with the natural alcohol (XXXVI) 39—46°, u.v., i.r., and n.m.r. spectra identical with those of the natural alcohol. The synthetic alcohol (28 mg) and  $\text{MnO}_2$  (400 mg) in Et<sub>2</sub>O (10 ml) gave needles (20 mg) of heptadeca-1,trans-7,trans-9-triene-11,13,15-triyn-6-one (XLVI), m.p. 106—108° (Found: C, 87.1; H, 7.3.  $\text{C}_{17}\text{H}_{16}\text{O}$  requires C, 86.5; H, 6.8%),  $\lambda_{\text{max}}$  (EtOH) 365 ( $\epsilon$  28 500), 340.5 (32 000), 325 (21 000), 305.5 (14 000), 283.5 (43 000), and 271.5 nm (29 500),  $\nu_{\text{max}}$  ( $\text{CHCl}_3$ ) 3 080, 1 835, and 920 ( $\text{CH=CH}_2$ ), 2 210 and 2 150 ( $\text{C}\equiv\text{C}$ ), 1 660 (CO), 1 640, 1 590, and 995  $\text{cm}^{-1}$  ( $\text{trans,trans-CH=CH}\cdot\text{CH=CH}$ ),  $\nu_{\text{max}}$  ( $\text{CS}_2$ ) 915  $\text{cm}^{-1}$ .

*Gerrie Hoek (Decorative, Pink).—Roots.* The tubers (8.4 kg; equiv. dry wt. 2.1 kg) contained the hydrocarbons (IX) (8 mg) and (XII) (60 mg), the acetates (XXVII) (55 mg) and (XXIX) (35 mg), and the alcohols (X) (30 mg), (XIII) (20 mg), and (XXVI) (930 mg).

*Roulette (Anemone-flowered).—Roots.* The tubers (350 g) contained the hydrocarbons (IV) (30 mg), (IX) (traces), and (XXXIX) (traces), the acetates (XXVII) (5 mg), (XXXI) (5 mg), and (XXIX) (30 mg), and the alcohols (XVI) (6 mg), (XXX) (5 mg), (XXVI) (1 mg), and (XXVIII) (1 mg). Traces of an ene-triyn-diene alcohol were not identified.

*Dolce vita (Colibri).—Roots.* The tubers (5.5 kg; equiv. dry wt. 1.1 kg) contained the hydrocarbons (IX) (ca. 1 mg) and (XV) (560 mg), the diacetate (XXIX) (2 mg), and the alcohols (XVI) (70 mg), (X) (6 mg), and (XXVIII) (100 mg).

*Flowers.* The dried flowers (220 g) contained the hydrocarbons (XXXV) (25 mg) and (IV) (40 mg) and the acetates (XXXVII) (3 mg) and (XXV) (235 mg).

*Leaves.* The dried leaves (340 g) contained the hydrocarbons (XXXV) (20 mg) and (IV) (0.5 mg) and the acetate (XXV) (50 mg) [traces of a triyne-diene acetate, presumably (XXXVII) were also present].

*Flocon de neige (Colibri).—Roots.* The tubers (6 kg; equiv. dry wt. 1.2 kg) contained the hydrocarbons (IX) (15 mg), an ene-tetrayn-ene, presumably (V) (traces), and (XV) (1.3 g), the acetates (XXVII) (10 mg), (XI) (6 mg),

<sup>14</sup> F. Bohlmann, U. Hinz, A. Seyberlich, and J. Repplinger, *Chem. Ber.*, 1964, **97**, 809.

<sup>15</sup> F. B. La Forge, N. Green, and W. A. Gersdorff, *J. Amer. Chem. Soc.*, 1948, **70**, 3707.

and (XXIX) (85 mg), and the alcohols (X) (60 mg), (XXVI) (40 mg), and (XXVIII) (10 mg).

*Flowers.* The dried flowers (140 g) contained the acetate (XXV) (25 mg) as the only polyacetylene. None was detected in the dried leaves (100 g).

*Investigation of the Seasonal Variation of Polyacetylenes in the Leaves of Dahlias.*—Leaves (30 g) picked at random from the plants (*D. coccinea*, species and garden variety,<sup>4</sup> and the hybrids Preference, Glorie van Heemstede, Roulette, Dolce vita, and Flocon de neige) at regular intervals from July 1 to September 30, were macerated and extracted with Me<sub>2</sub>CO. The extracts were transferred into Et<sub>2</sub>O and the polyacetylene contents of separate fractions obtained on chromatography were estimated from the u.v. spectra.

*Analysis of the Polyacetylene Content of Dahlia Seedlings.*—Seeds of *D. scapigera*, *D. coccinea*, and several garden varieties (Pomponne, Collarette, Cactus, Coltness Gem, and

Carter's Goliath Strain) were allowed to germinate in the dark on wet tissue paper for 6 days. (Polyacetylene spectra could often be recognised with as few as 12 seedlings.) The seedlings were extracted with Et<sub>2</sub>O, the extract was checked by u.v. and chromatographed, and the fractions were analysed by u.v. spectroscopy again. From a large batch of Cactus seedlings (*ca.* 1 000), the main fraction had  $\lambda_{\text{max}}$  390, 360, 335, 313, 286, 270, and 258 nm,  $\nu_{\text{max}}$  (CCl<sub>4</sub>) 2 200, 1 750, 1 695, 950, and 920 cm<sup>-1</sup>, and could not be distinguished by t.l.c. (CH<sub>2</sub>Cl<sub>2</sub>-petrol, 7:5) from the C<sub>13</sub> acetate (VIII) ( $R_F$  0.48).

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