Natural Acetylenes. Part XXXI.[1] C_{14}-Tetrahydropyranyl and other Polyacetylenes from the Compositae *Dahlia coccinea* Cav. var. *coccinea* [2]

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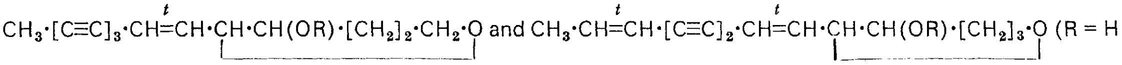
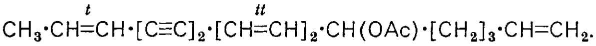
The polyacetylene contents of one form of the species *Dahlia coccinea* Cav. var. *coccinea* and also of a horticultural form derived from the same species have been examined. The nineteen polyacetylenes detected comprised eight C_{13}, eight C_{14}, and three C_{17} compounds. Five of them were previously unknown; their isolation, characterisation, and structure determination are described. They are the C_{14} 2,3-disbustituted tetrahydroprans



$CH_3\cdot[C\equiv C]_3\cdot CH\overset{t}{=}CH\cdot\underline{CH\cdot CH(OR)\cdot[CH_2]_2\cdot CH_2\cdot O}$ and $CH_3\cdot CH\overset{t}{=}CH\cdot[C\equiv C]_2\cdot CH\overset{t}{=}CH\cdot\underline{CH\cdot CH(OR)\cdot[CH_2]_3\cdot O}$ (R = H or Ac), and the C_{17} acetate



$CH_3\cdot CH\overset{t}{=}CH\cdot[C\equiv C]_2\cdot[CH\overset{tt}{=}CH]_2\cdot CH(OAc)\cdot[CH_2]_3\cdot CH=CH_2$.

SÖRENSEN[3] was the first to report the presence of a polyacetylene, the C_{13} hydrocarbon (I), in the genus *Dahlia* (*Heliantheae* tribe, family Compositae) and screening of root extracts of plants belonging to this genus by u.v. spectroscopy revealed in every case the presence of polyacetylenes, sometimes in large amounts. A more detailed study of the polyacetylene content of several representatives of this genus was then undertaken,[4] primarily with biosynthetic objectives (*cf.* ref. 5).

The advice of Dr. E. E. Sherff † on colour slides and herbarium specimens ‡ of the plants we examined was invaluable. There was some initial confusion regarding *Dahlia coccinea* and *Dahlia Merckii* in earlier publications [2a,4] prior to Dr. Sherff's identification of these species as *Dahlia coccinea* Cav. var. *coccinea* and *Dahlia scapigera* Link and Otto var. *scapigera* f. *scapigera*, respectively. The polyacetylenes found in the two species and several garden varieties investigated will be described in this and subsequent papers.

A form of the species *Dahlia coccinea* Cav. var. *coccinea*,[6] propagated from seeds collected in Mexico, and what Dr. Sherff recognised as a horticultural form § of the same species, were grown in an Oxford garden. The flowers of the species were yellow, orange, or orange-red; those of the garden variety were deep purple. A purple pigment was also evident in the leaves and stems of the hybrid. The plants were harvested in October: the tuberous roots were extracted fresh with acetone, and the leaves and flowers were dried at room temperature and extracted with ether. Sun-dried flowers of the species were obtained from Mexico. The extracts were separated into fractions according to polarity and chromophores by repeated column chromatography and, where necessary, t.l.c. No attempts were made to isolate those compounds which occurred in small amounts and could almost certainly be identified as known polyacetylenes on the basis of their spectra and chromatographic behaviour. The concentrations of the individual polyacetylenes in mg./kg. dry material [the roots ~80% water] have been calculated from the appropriate known u.v. ε values and are given in Table 1.

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† Author of the Dahlia section in 'North American Flora.'

‡ Deposited in the Fielding–Druce Herbarium, OXF.

§ In the summary of this work (ref. 4) we were under the erroneous impression that this garden variety was a species, which was referred to as *Dahlia liciniata purpurea*.

[1] Part XXX, R. K. Bentley, Sir Ewart R. H. Jones, and V. Thaller, *J. Chem. Soc.* (*C*), 1969, 1096.

[2] Preliminary communications: (*a*) C. Chin, Sir Ewart R. H. Jones, and V. Thaller; R. T. Aplin, L. J. Durham, S. C. Cascon, W. B. Mors, and B. M. Tursch, *Chem. Comm.*, 1965, 152; (*b*) C. Chin, M. C. Cutler, J. Lee, and V. Thaller, *Chem. Comm.*, 1966, 202.

[3] N. A. Sörensen, Centenary Lecture, *Proc. Chem. Soc.*, 1961, 98, and private communication.

[4] For summary see Sir Ewart R. H. Jones, *Chem. Brit.*, 1966, 2, 6.

[5] J. R. F. Fairbrother, Sir Ewart R. H. Jones, and V. Thaller, *J. Chem. Soc.* (*C*), 1967, 1035; Sir Ewart R. H. Jones, S. Safe, and V. Thaller, *J. Chem. Soc.* (*C*), 1967, 1038.

[6] J. Lam, F. Kaufmann, and O. Bendixen, *Phytochemistry*, 1968, 7, 269, also studied plants of this species.

The most striking structural feature of the compounds occurring in the roots is the universal presence of the terminal propenyl group in contrast to the corresponding propynyl group in the leaves and flowers. Considerable variations in polyacetylene content and composition were encountered within the species or garden variety in consecutive seasons, in the same season in plants in different growing locations and at different stages of growth (this is discussed in another paper). It is therefore hardly surprising that Lam *et al.*[6] found different polyacetylene compositions for *Dahlia coccinea* strains, and that these results also differed from ours. The Danish workers also mentioned the absence of polyacetylenes in *Dahlia imperialis*: we found in preliminary investigations of the genus *Dahlia* in the roots of this species (extracted in auyumn before flowering occurred) a small amount (*ca.* 20 mg./kg. of fresh tubers) of polyacetylenes with ene-tetrayn-ene and diene-triyn-ene chromophores.

TABLE 1

Concentrations of individual polyacetylenes (in mg./kg. dry weight)

		Species		Hybrid		Ref.
	Roots					
(I)	$CH_3{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_4{\cdot}CH{=}CH_2$	*ca.* 0·5		5		*a*
(II)	$HOCH_2{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_4{\cdot}CH{=}CH_2$	15				20
(IIa)	$AcO{\cdot}CH_2{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_4{\cdot}CH{=}CH_2$	2·5				20
(III)	$CH_3{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_3{\cdot}[CH\overset{t}{=}CH]_2H$			10		30
(IV)	$HOCH_2{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_3{\cdot}[CH\overset{t}{=}CH]_2H$	15		15		21
(IVa)	$AcO{\cdot}CH_2{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_3{\cdot}[CH\overset{t}{=}CH]_2H$	5		5		21
(V)	$CH_3{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}C_6H_5$			1250		30
(VI)	$CH_3{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}[CH\overset{tt}{=}CH]_2{\cdot}CH(OAc){\cdot}CH_2{\cdot}CH_2{\cdot}OAc$			200		31
(VII)	$CH_3{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}CH\overset{t}{=}CH{\cdot}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O$			75		
(VIIa)	$CH_3{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}CH\overset{t}{=}CH{\cdot}CH{\cdot}CH(OAc){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O$			375		
(VIII)	$CH_3{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}[CH\overset{tt}{=}CH]_2{\cdot}[CH_2]_4{\cdot}CH{=}CH_2$			150		29
(IX)	$CH_3{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}[CH\overset{tt}{=}CH]_2{\cdot}CH(OAc){\cdot}[CH_2]_3{\cdot}CH{=}CH_2$			25		
	Leaves and flowers	Leaves	Flowers	Leaves	Flowers	
(X)	$CH_3{\cdot}[C{\equiv}C]_3{\cdot}C_6H_5$			1	1	33
(XI)	$CH_3{\cdot}[C{\equiv}C]_3{\cdot}[CH\overset{tt}{=}CH]_2{\cdot}[CH_2]_2{\cdot}CH_2OH$	30	25			*b*
(XIa)	$CH_3{\cdot}[C{\equiv}C]_3{\cdot}[CH\overset{tt}{=}CH]_2{\cdot}[CH_2]_2{\cdot}CH_2OAc$	<1	5			*c*
(XII)	$CH_3{\cdot}[C{\equiv}C]_3{\cdot}[CH\overset{tt}{=}CH]_2{\cdot}CH(OAc){\cdot}CH_2{\cdot}CH_2OAc$	25	20			22
(XIII)	$CH_3{\cdot}[C{\equiv}C]_3{\cdot}CH\overset{t}{=}CH{\cdot}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O$	200	160		75	
(XIIIa)	$CH_3{\cdot}[C{\equiv}C]_3{\cdot}CH\overset{t}{=}CH{\cdot}CH{\cdot}CH(OAc){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O$	2500	250		110	
(XIV)	$CH_3{\cdot}[C{\equiv}C]_3{\cdot}[CH\overset{tt}{=}CH]_2{\cdot}[CH_2]_4{\cdot}CH{=}CH_2$			20	50	32

[a] J. S. Sörensen and N. A. Sörensen, *Acta Chem. Scand.*, 1954, **8**, 1741. [b] F. Bohlmann, W. von Kap-herr, L. Fanghänel, and C. Arndt, *Chem. Ber.*, 1965, **98**, 1411. [c] F. Bohlmann, C. Arndt, and H. Bornowski, *Chem. Ber.*, 1960, **93**, 1937.

Species.—The polyacetylene content of the roots was rather low. It amounted in the large scale experiment described to about 10 mg./kg. of fresh roots. Two chromophores only were present, ene-tetrayn-ene and ene-triyne-diene. They were found to belong to five known C_{13} compounds, the hydrocarbon (I), the acetates (IIa) and (IVa), and the alcohols (II) and (IV).

The polyacetylenes from both the leaves and flowers, although the quantities were different, proved to be identical. Three of them, occurring in low concentrations, were the known C_{14} triyne-diene monoacetate (XIa), diacetate (XII), and alcohol (XI). The main polyacetylenic constituents of both extracts were a triyn-ene acetate (XIIIa) and its alcohol (XIII), and since they could not be identified with known compounds, their structures were investigated.

Both compounds were crystalline and optically active and their alcohol–acetate relationship was readily established. They gave the same u.v. spectrum, identical to that[7] of *trans*-dehydromatricarianol (XV); bands in the 950 cm.$^{-1}$ region confirmed the *trans*-configuration of the double bond. Analysis together with osmometric and mass-spectrometric

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[7] J. N. Gardner, E. R. H. Jones, P. R. Leeming, and J. S. Stephenson, *J. Chem. Soc.*, 1960, 691.

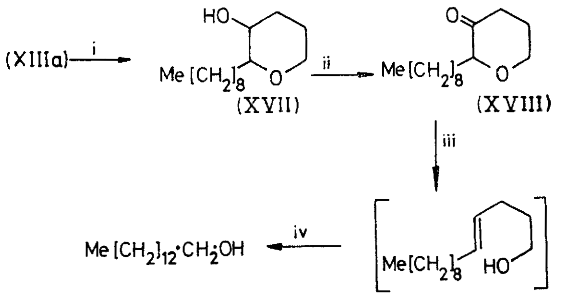
molecular weight determinations gave the molecular formula $C_{14}H_{14}O_2$ for the alcohol. The latter could not be oxidised by manganese dioxide nor by

$$\mathrm{Me[C{\equiv}C]_3{\cdot}CH\overset{t}{=}CHR}$$

$$\mathrm{(XV)\ R = CH_2OH \quad (XVI)\ R = CO_2Me}$$

chromic acid in pyridine, but surprisingly, with 8N-chromic acid in acetone at 5°, it was degraded to dehydromatricaria acid, isolated as its methyl ester (XVI) in 22% yield.

Oxidation of the saturated alcohol (XVII), from catalytic hydrogenation of the acetate (XIIIa) (uptake 7 mol. of hydrogen) followed by alkaline hydrolysis, yielded a saturated ketone (XVIII), still optically active. All compounds, unsaturated and saturated, showed multiple band absorption in the 1100 cm.$^{-1}$ region (C–O–C). This, together with the chemical behaviour mentioned and the n.m.r. spectra (see later), suggested a 2-substituted tetrahydropyran structure with the hydroxy-group in a position which, on oxidation, would permit easy degradation to dehydromatricaria acid. The production of n-tetradecanol (50% yield) on Wolff–Kishner reduction of the saturated ketone (XVIII) followed by catalytic hydrogenation, indicated that it was an α-substituted ketone (similarly α-substituted ketones were found to give unsaturated compounds when subjected to Huang–Minlon reduction [8]), *i.e.* 2-nonyltetrahydropyran-3-one.



SCHEME 1

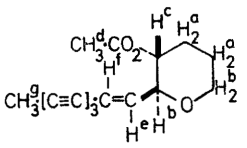
Reagents: i, H_2–Rh, HO^-; ii, CrO_3–Me_2CO; iii, Huang–Minlon; iv, H_2–Pd

^{1}H N.m.r. spectra (60 MHz) (Table 2) supported this assignment. However, the τ 5—7 region (4H), which was of great interest because of the information it could give about the position of the acetoxy-group, was very complex; it could be interpreted only at a later stage when the alcohol (XIII) (named ichthyotherol) and the acetate (XIIIa) were isolated from *Ichthyothere terminalis* (Spreng.) and the 100 MHz double resonance spectra became available.[2a, 9] The structural studies on ichthyotherol, mainly interpretations of n.m.r. and mass spectra, were largely complementary to our work. We have avoided wherever possible description and discussions of data already published in full by the American authors.[9]

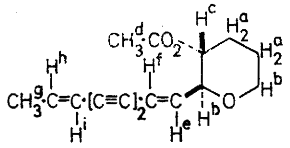
The presence of a 2,3-disubstituted tetrahydropyranyl system received confirmation from the ozonolysis results, and was proved by the synthesis of the racemic saturated ketone (XVIII). Ozonolysis of the acetate (XIIIa) in methanol at —70°, cleavage of the methoxyhydroperoxide with trimethyl phosphite,[10] and repeated chromatography on silica gel resulted in the isolation of four fractions. Octa-2,4,6-triynal (XIX) and its hemiacetal (XXI) were identified by their u.v. and i.r. spectra. The most polar fraction was optically active, and showed only end absorption in the u.v. and bands in the i.r. indicating an acetoxy- and an aldehyde group (1740, 1370, and 1050 cm.$^{-1}$) and the tetrahydropyran ring system (1100 and 1080 cm.$^{-1}$). The fourth fraction is a transformation product of the most polar fraction, generated during chromatography, in unsuccessful attempts to purify the most polar fraction. The artefact, no longer optically active, absorbing at 254 nm. and at 1700, 1640, and 940 cm.$^{-1}$ is clearly the unsaturated aldehyde (XXII) formed by elimination from the acetoxy-aldehyde (XX).

TABLE 2

Correlation of chemical shifts (τ) and coupling constants (*J* in Hz) for the acetates (XIIIa) and (VIIa) (60 MHz) in $CDCl_3$

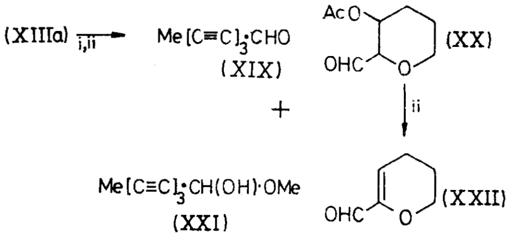


(XIIIa)



(VIIa)

H		
a	7·6—8·3 (m)	7·6—8·3 (m)
b	5·8—6·8 (m)	5·8—6·8 (m)
c	5·45 (dt, 4—4·5 and 9—10)	5·43 (dt, 4—5 and 9—10)
d	7·95 (s)	7·96 (s)
e	3·62 (dd, 16 and 5·5)	3·72 (dd, 16 and 5·5)
f	4·20 (dd, 16 and 1·5)	4·18 (dd, 16 and 1·5)
g	8·03 (s)	8·16 (dd, 6 and 1·5)
h		3·64 (dq, 16 and 6)
i		4·42 (dq, 16 and 1)



SCHEME 2

Reagents: O_3–MeOH, $(MeO)_3P$; ii, SiO_2-chromatography

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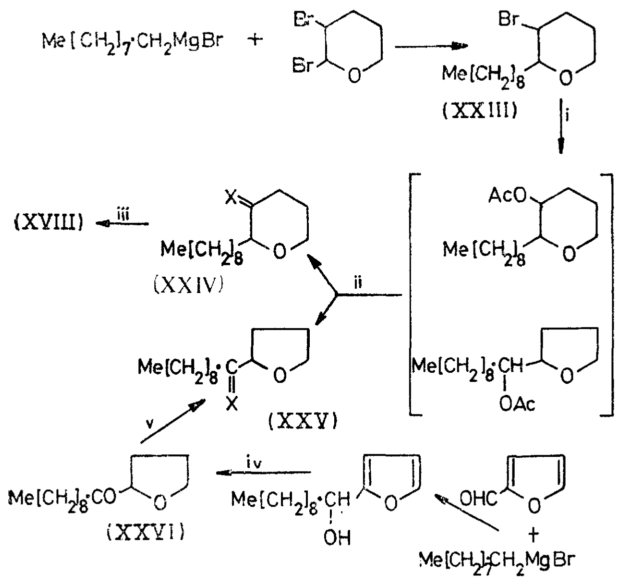
[8] N. J. Leonard and S. Gelfand, *J. Amer. Chem. Soc.*, 1955, **77**, 3269; P. S. Wharton, S. Dunny, and L. S. Krebs, *J. Org. Chem.*, 1964, **29**, 958.

[9] S. C. Cascon, W. B. Mors, B. M. Tursch, R. T. Aplin, and L. J. Durham, *J. Amer. Chem. Soc.*, 1965, **87**, 5237.

[10] W. S. Knowles and Q. E. Thompson, *J. Org. Chem.*, 1960, **25**, 1031.

For the synthesis of the ketone (XVIII), 3-bromo-2-nonyltetrahydropyran (XXIII), prepared by Paul's method[11] was converted[12] into a mixture of acetates, inseparable by chromatography. After hydrolysis and oxidation 2,4-dinitrophenylhydrazones were made which could be separated by chromatography. The less polar derivative (XXV) was identical to that of 2-n-decanoyltetrahydrofuran (XXV) synthesised by another route for mass spectral studies.[9] The more polar dinitrophenylhydrazone (XXIV) on refluxing with laevulic acid,[13] gave the racemic form of the desired ketone (XVIII) with spectral and chromatographic properties identical to those of the perhydro-ketone (XVIII) from the natural tetrahydropyranyl acetate (XIIIa).



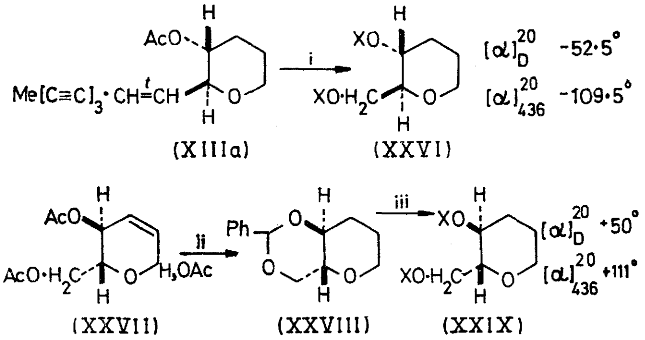
$X = 2,4\text{-}(NO_2)_2C_6H_3\cdot NH\cdot N<$

SCHEME 3

Reagents: i, AgOAc–AcOH; ii, HO$^-$, CrO_3–Me_2CO, XH_2,HCl, SiO_2-chromatography; iii, laevulic acid (reflux); iv, H_2–Pd, CrO_3–Me_2CO; v, XH_2,HCl

The conversion of both tetrahydrofurfuryl bromide and tosylate into a mixture of tetrahydrofurfuryl alcohol and 3-hydroxytetrahydropyran on hydrolysis has been reported.[14] The formation of the tetrahydrofurfuryl acetate from the 3-bromotetrahydropyran is probably analogous: neighbouring group participation of the ether oxygen with the incipient carbonium ion generated by the action of the silver ion on the bromine atom gives the acetate ion an opportunity to attack in either position 2 (tetrahydrofurfuryl product) or position 3 (tetrahydropyranyl product).

The relative configuration of the substituents on the tetrahydropyranyl ring in the natural compounds followed from n.m.r. studies at 100 MHz.[2a,9] Both substituents were found to be equatorial and hence *trans*. This was confirmed and, in addition, the absolute configuration of the tetrahydropyran was determined, by comparing it with a compound of known absolute configuration.[2b] To this end the acetate (XIIIa) was ozonised in methanol and the ozonide was cleaved to the alcohols by sodium borohydride reduction,[15] thus avoiding the formation of the unstable aldehyde (XX). Alkaline hydrolysis followed by dinitrobenzoyl chloride–pyridine treatment yielded the bisdinitrobenzoyl ester (XXVI) which could be purified to constant optical activity by repeated chromatography and crystallisation.[16] A corresponding *trans*-tetrahydro-3-hydroxy-2-hydroxymethylpyran (characterised as its benzylidene derivative) was synthesised by Bergmann[17] from triacetyl-D-pseudoglucal (XXVII), which Fischer[18] prepared from D-glucose. Fischer's and Bergmann's procedures were followed with some modifications. The benzylidene derivative (XXVIII) was purified and crystallised to constant optical activity, hydrolysed, and converted into the bisdinitrobenzoyl derivative (XXIX). The two esters, (XXVI) and (XXIX), had identical m.p.s, i.r. spectra, and mass spectra, and opposite specific rotations. The absolute configuration of the natural acetate (XIIIa) is therefore the mirror image of that of the ester (XXIX).



X = 3,5-dinitrobenzoyl

SCHEME 4

Reagents: O_3–MeOH, $NaBH_4$, HO$^-$, XCl–Py; ii, H_2–Pd, HO$^-$, PhCHO–$ZnCl_2$; iii, H$^+$, XCl–Py

Hybrid.—The polyacetylene content of the hybrid differed considerably from that of the species. Especially noticeable was the absence of the acetate (XIIIa) and alcohol (XIII) in the leaves; however, in the flowers these compounds were present in amounts comparable to those from the species.

The roots contained a greater variety and higher concentration of polyacetylenes than the roots of the species.

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[11] R. Paul, *Bull. Soc. chim. France*, 1935 [5], **2**, 311.

[12] H. L. Slates and N. L. Wendler, *J. Amer. Chem. Soc.*, 1956, **78**, 3749.

[13] C. H. De Puy and B. W. Ponder, *J. Amer. Chem. Soc.*, 1959, **81**, 4629.

[14] D. Cagnaire, *Compt. rend.*, 1959, **248**, 420.

[15] J. B. Patrick and B. Witkop, *J. Org. Chem.*, 1954, **19**, 1824; J. A. Sousa and A. L. Bluhm, *J. Org. Chem.*, 1960, **25**, 108.

[16] A. S. Matthews, W. G. Overend, F. Shafizadeh, and M. Stacey, *J. Chem. Soc.*, 1955, 2511, described the 3,5-dinitrobenzoyl ester of a tetrahydro-3-hydroxy-2-hydroxy-methylpyran of unidentified stereochemistry.

[17] M. Bergmann and W. Breuers, *Annalen*, 1929, **470**, 51.

[18] E. Fischer, *Chem. Ber.*, 1914, **47**, 196.

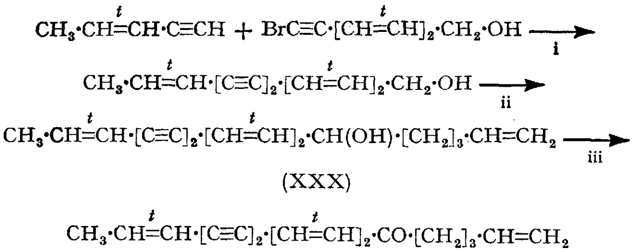
The largest single component was the phenylheptenediyne (V). Four other C_{13} polyacetylenes, the ene-tetrayn-ene (I) and ene-triyne-diene (III) hydrocarbons, and the ene-triyne-diene acetate (IVa) and alcohol (IV), were present in small amounts, and the C_{14} ene-diyne-diene diacetate (VI) and C_{17} hydrocarbon (VIII) were found in moderate quantities. Two new ene-diyn-ene compounds, one present in moderate quantity, and a new ene-diyne-diene acetate, were shown to be the acetate (VIIa) and its alcohol (VII), and the acetate (IX).

The acetate (VIIa) considerably resembled the tetrahydropyranyl acetate (XIIIa) in its i.r. spectrum (triad at 1105, 1085, and 1075 cm.$^{-1}$) and optical rotation, and the alcohols showed corresponding similarities. It was soon obvious that the acetate (VIIa) differed from that (XIIIa) from the species *Dahlia* only in its chromophore, being the dihydro-derivative of the latter. This was confirmed by n.m.r. and mass spectral studies, as well as comparative g.l.c.

The 60 MHz n.m.r. spectra of the two acetates (VIIa) and (XIIIa) are in Table 2; the τ values and coupling constants are in complete agreement.

The mass spectra of the alcohols (VII) and (XIII) showed the expected differences. The identity of the *m/e* 100 and 71 peaks, the difference of two mass units for the molecular ions (*m/e* 216 and 214) and the *m/e* 145 and 143 peaks, confirm both the relationship of the two compounds and the fragmentation pattern proposed for the tetrahydropyranyl part of the triyn-ene alcohol (XIII).[9]

The chromatographic behaviour of the new ene-diyne-diene (IX), available in only very small quantities, suggested that it was an acetate. This was confirmed by its i.r. spectrum which also showed the presence of a terminal ethylenic bond and the 'all-*trans*' configuration of the double bonds. The corresponding alcohol (XXX) with manganese dioxide gave a ketone, proving the allylic nature of the hydroxy-group, and this on hydrogenation gave 6-hydroxyheptadecane.* The structure of the new product was finally established by the synthesis shown in Scheme 5.



$$\mathrm{CH_3{\cdot}CH\overset{t}{=}CH{\cdot}C{\equiv}CH + BrC{\equiv}C{\cdot}[CH\overset{t}{=}CH]_2{\cdot}CH_2{\cdot}OH} \xrightarrow[\text{i}]{}$$

$$\mathrm{CH_3{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}[CH\overset{t}{=}CH]_2{\cdot}CH_2{\cdot}OH} \xrightarrow[\text{ii}]{}$$

$$\mathrm{CH_3{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}[CH\overset{t}{=}CH]_2{\cdot}CH(OH){\cdot}[CH_2]_3{\cdot}CH{=}CH_2} \xrightarrow[\text{iii}]{}$$

(XXX)

$$\mathrm{CH_3{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}[CH\overset{t}{=}CH]_2{\cdot}CO{\cdot}[CH_2]_3{\cdot}CH{=}CH_2}$$

(XXXI)

SCHEME 5

Reagents: i, Cu_2Cl_2, $EtNH_2$, $H_2N{\cdot}OH$; ii, MnO_2, $BrMg(CH_2]_3{\cdot}CH{=}CH_2$; iii, MnO_2

The leaves were very poor in polyacetylenes and only the two hydrocarbons, the phenylheptatriyne (X) and the C_{17} triyne-diene (XIV), were detected. These appeared also in the flowers, which in addition contained the acetate (XIIIa) and the alcohol (XIII).

EXPERIMENTAL

Equipment: u.v., Carey M14 and Unicam SP 800; i.r., Perkin-Elmer 237 and Unicam SP 200; n.m.r., Perkin-Elmer R10; mass spectra (direct insertion), A.E.I. MS9; optical rotation, E.T.L.–N.P.L. 143A and Perkin-Elmer 141; molecular weight, Mechrolab Osmometer 301; m.p. (corr.), Kofler hot-stage apparatus.

Liquid chromatography: silica gel Whatman SG 31 in columns and Merck HF and HF_{254} in 0·3 and 1 mm. layers; alumina Spence grade H (neutralised and deactivated with 5% H_2O) in columns. Gas chromatography: Apiezon L (10%) on Embacel (1200 × 4·5 mm.) with argon.

Light petroleum refers to fraction b.p. 40—60°. Manganese dioxide was freshly prepared.[19] All evaporations of solutions containing acetylenic compounds were carried out under reduced pressure below 40°.

Species

Isolation of the Polyacetylenes from the Roots.—The tubers (31 kg.) were minced and extracted with acetone at 20°; the extract was decanted and fresh acetone was added several times. The combined extracts were concentrated until water began to distil off; the residual liquid was diluted with an equal volume of water, saturated with sodium chloride, and extracted with ether. The ethereal extract was dried and concentrated. The residue (12 g.) contained polyacetylenic material (estimated *ca.* 350 mg.) with ene-tetrayn-ene and diene-triyn-ene chromophores and was chromatographed on a silica gel column (250 g.) with light petroleum–ether mixtures: 20% ether eluted a hydrocarbon fraction, 30% ether an acetate fraction, and 60—100% ether eluted an alcohol fraction. The hydrocarbon fraction showed only an ene-tetrayn-ene chromophore; the corresponding polyacetylene was not isolated, but a g.l.c. peak from the hydrogenated sample had the same R_t value as n-tridecane and indicated the presence of hydrocarbon (I) (3 mg.). The acetates were separated on silica gel impregnated with silver nitrate (10%). Two polyacetylene fractions were obtained: the faster moving was the acetate (IIa) (7 mg.) and the slower was the acetate (IVa) (15 mg.); both were hydrolysed to the corresponding alcohols (II) and (IV). The alcohol fraction yielded on repeated chromatography the crystalline alcohols (II) (80 mg.) and (IV) (80 mg.). Both had m.p.s, spectra data, and reactions identical with those described.[20,21]

Isolation of the Polyacetylenes from the Leaves.—The dried, milled leaves (2 kg.) were extracted with several batches of ether at 20°. The combined extracts were concentrated and the residue (46 g.) was digested repeatedly with methanol–water (8 : 2 and 9 : 1 respectively) leaving behind the bulk of non-polyacetylenic material. Most of the methanol was

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* We thank Prof. F. L. Breusch, University of Istanbul, for samples of hydroxyheptadecanes, which were oxidised where necessary to the corresponding ketones.

[19] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1952, 1094.

[20] F. Bohlmann, Ch. Arndt, H. Bornowski, and K.-M. Kleine, *Chem. Ber.*, 1962, **95**, 1315.

[21] F. Bohlmann, H. Bornowski, and S. Köhn, *Chem. Ber.*, 1964, **97**, 2583.

evaporated from the combined extracts and the predominantly aqueous solution left was saturated with sodium chloride and extracted with ether. The residue (14 g.) from the ether extract was separated on silica gel (800 g.) by gradient elution chromatography from light petroleum–ether into four fractions (A, B, C, and D).

The least polar polyacetylene, most likely the acetate (XIa) (the corresponding alcohol is present in fraction D), appeared in fraction A only in traces, together with a large amount of non-acetylenic material.

Fraction B showed very intense triyn-ene absorption belonging to one component (*ca.* 5 g.). Rechromatography on silica gel and alumina followed by crystallisation from light petroleum yielded needles of (2S,3R)-*tetrahydro*-2-(*non*-trans-1-*ene*-3,5,7-*triynyl*)*pyran*-3-*yl acetate* (XIIIa) (4·2 g.), m.p. 64—64·5° [Found: C, 74·75; H, 6·45%; *M* (osmometer), 255. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%; *M*, 256]; $[\alpha]_D^{20\cdot5}$ +26 ± 1° (*c* 0·2435 in CCl_4) and +6·5 ± 1·5° (*c* 0·201 in $CHCl_3$); $\lambda_{\text{max.}}$ (EtOH) 330 (ε 15,500), 308 (22,400), 289 (16,900), 273 (9200), 258 (4900), 243·5 (114,000), and 231·5 (73,500) nm., $\nu_{\text{max.}}$ (CCl_4) 2230 and 2210 (C≡C), 1750, 1370, 1230 and 1045 (OAc), 1120, 1100 and 1075 (substituted tetrahydropyran), and 955 and 945 (*trans*-CH=CH) cm.$^{-1}$, $\nu_{\text{max.}}$ (CS_2) 1750, 1375, 1230 and 1045 (OAc), 1110, 1100 and 1075 (substituted tetrahydropyran), and 955 and 945 (*trans*-CH=CH) cm.$^{-1}$; for n.m.r. see Table 2. Acidic and alkaline hydrolysis gave the alcohol (XIII) (see later).

Fraction C (1·25 g.) was separated on alumina (20 g.) and a fraction (210 mg.) was obtained which contained the diacetate (XII) (*ca.* 45 mg.) as the major polyacetylene. Crystallisation was not attempted as it had R_F values identical with those of an authentic specimen of the diacetate (XII), and the perhydro-compound and 1,3-diacetoxy-n-tetradecane had identical R_t values. The non-crystalline parent alcohol obtained from the diacetate (XII) by hydrolysis at 20° showed the spectra and chemical behaviour described.[22]

Fraction D (2 g.) was rechromatographed on alumina. The less polar, predominantly triyn-ene fraction (700 mg. containing *ca.* 400 mg. polyacetylenic material), solidified and was recrystallised (ether–light petroleum) to yield micro-needles of (2S,3R)-*tetrahydro*-2-(*non*-trans-1-*ene*-3,5,7-*triynyl*)*pyran*-3-*ol* (XIII), m.p. 88—89° [Found: C, 78·3; H, 6·7%; *M* (osmometer), 214. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%; *M*, 214]; $[\alpha]_D^{21}$ −40 ± 1° (*c* 0·231 in $CHCl_3$) and −50 ± 1° (*c* 0·2175 in CCl_4), $\lambda_{\text{max.}}$ (EtOH) 329·5 (ε 16,000), 308·5 (23,800), 289·5 (17,000), 273 (9300), 257·5 (6700), 244·5 (80,000), and 233 (62,000) nm., $\nu_{\text{max.}}$ (CS_2) 3600 (OH), 1120sh, 1100sh and 1090 (tetrahydropyran), and 950 and 935 (*trans*-CH=CH) cm.$^{-1}$, $\nu_{\text{max.}}$ ($CHCl_3$) 3590 and 3400 (OH), 2200 (C≡C), 1085 (tetrahydropyran), and 955 and 935 (*trans*-CH=CH) cm.$^{-1}$, τ ($CDCl_3$) 8·03 (s, MeC≡C), 7·83 (s, OH), 7·8—8·3 [m, $OCH_2\cdot[C\mathit{H}_2]_2\cdot CH\cdot OH$], 5·7—7·0 (m, $C\mathit{H}_2\cdot O\cdot C\mathit{H}$ and HOC*H*), 4·15 (dd, *J* 16 and 1·5 Hz, *trans*-C*H*=CH·CH), and 3·55 (dd, *J* 16 and 5 Hz, *trans*-CH=C*H*·CH). Acetylation with acetic anhydride–pyridine gave the acetate (XIIIa).

The more polar part of fraction D (570 mg.) contained only one chromophore, most likely the alcohol (XI) (*ca.* 60 mg.). Neither the alcohol nor the corresponding acetate (XIa) crystallised after repeated chromatography. The latter and an authentic specimen of the acetate (XIa) had identical R_F values and the fully hydrogenated product and n-tetradecanol acetate had identical R_t values.

Isolation of the Polyacetylenes from the Flowers.—The dried, milled flowers (156 g.) were extracted with ether. The extract (7·1 g., containing *ca.* 100 mg. polyacetylenes) was separated by gradient elution chromatography (see extraction from leaves) into four fractions which were analysed and appeared to contain the same polyacetylenes as the corresponding leaf-fractions; again, only the acetate (XIIIa) and the alcohol (XIII) were obtained crystalline.

Oxidation of the Alcohol (XIII) *to Dehydromatricaria Ester* (XVI).—The alcohol (XIII) (150 mg.) was treated in acetone (30 ml.) with an excess of 8N-chromic acid (2 ml.) with stirring under nitrogen at 5°. The products were transferred to ether and the ethereal solution was extracted with sodium hydrogen carbonate solution. The latter was acidified and extracted with ether, yielding an ethereal solution of dehydromatricaria acid. This was concentrated and the residue was kept for 18 hr. in 3% methanolic sulphuric acid (25 ml.). Isolation with ether and chromatography on silica gel gave *trans*-dehydromatricaria ester (XVI) (27 mg., 22·5%), which crystallised from light petroleum in pale yellow needles (9 mg.); m.p. and u.v. spectrum were identical with those reported.[23]

(2S,3R)-*Tetrahydro*-2-(*n-nonyl*)*pyran*-3-*ol* (XVII) *and its Acetate.*—The acetate (XIIIa) (274 mg.) in ethanol (30 ml.) was hydrogenated over 5% rhodium–charcoal (104 mg.). Evaporation of the solvent left (2S,3R)-*tetrahydro*-2-(*n-nonyl*)*pyran*-3-*yl acetate*, b.p. 120° (block)/0·3 mm. (Found: C, 71·25; H, 11·2%; M^+, 270. $C_{16}H_{30}O_3$ requires C, 71·1; H, 11·2%; *M*, 270); $[\alpha]_D^{22}$ −44 ± 0·5° (*c* 0·794 in CCl_4), $\nu_{\text{max.}}$ (CCl_4) 1750, 1375, 1235 and 1035 (OAc), and 1100 (tetrahydropyran) cm.$^{-1}$. The perhydro-acetate (627 mg.) in methanol (30 ml.) and aqueous potassium hydroxide (15%; 20 ml.) was refluxed for 1 hr. Removal of the methanol followed by ether extraction yielded (2S,3R)-*tetrahydro*-2-(*n-nonyl*)*pyran*-3-*ol* (XVII), b.p. 140° (block)/0·2 mm. (Found: C, 73·4; H, 12·2%; M^+, 228. $C_{14}H_{28}O_2$ requires C, 73·6; H, 12·4%; *M*, 228), $[\alpha]_D^{22}$ −42 ± 0·5° (*c* 0·5205 in CCl_4), $\nu_{\text{max.}}$ (CCl_4) 3640 (OH) and 1100 and 1050 (tetrahydropyran) cm.$^{-1}$.

(2S)-*Tetrahydro*-2-(*n-nonyl*)*pyran*-3-*one* (XVIII) *and its Reduction to n-Tetradecanol.*—The alcohol (XVII) (290 mg.) was oxidised with chromic acid in acetone nearly quantitatively to (2S)-*tetrahydro*-2-(*n-nonyl*)*pyran*-3-*one* (XVIII), b.p. 100° (block)/0·07 mm., $[\alpha]_D^{22}$ −28·5 ± 0·5° (*c* 1·0505 in CCl_4), $\nu_{\text{max.}}$ (CCl_4) 1730 (CO) and 1107 (tetrahydropyran) cm.$^{-1}$, M^+ 226, τ ($CDCl_3$) 9·12 (t, *J* 5—6 Hz, $C\mathit{H}_3[CH_2]_n$), 8·72br ($[CH_2]_n$), 7·8—8·1 (m, $CO\cdot CH_2\cdot C\mathit{H}_2$), 7·4—7·8 (m, $CO\cdot C\mathit{H}_2\cdot CH_2$), and 5·75—6·60 (m, $C\mathit{H}\cdot O\cdot C\mathit{H}_2$). The ketone gave a 2,4-*dinitrophenylhydrazone*, m.p. 88—89° (Found: C, 58·65; H, 7·5; N, 14·25. $C_{20}H_{30}N_4O_5$ requires C, 59·1; H, 7·45; N, 13·8%).

The tetrahydropyranone (85 mg.), hydrazine hydrate (85%, 0·2 ml.), potassium hydroxide (0·4 g.) and diethylene glycol (10 ml.) were refluxed for 1·5 hr. Water was then distilled off until the temp. of the mixture reached 180—190°, and the remaining solution was refluxed for 4 hr. The mixture was extracted with ether, the extract was concentrated, and the residue (26 mg.) was hydrogenated over 5% palladium–charcoal. One of the products (*ca.* 50% of the sample) had the same R_t value (15 min. at 170°) as n-tetradecanol.

Ozonolysis of the Acetate (XIIIa).—This (256 mg.) in

[22] F. Bohlmann and K.-M. Kleine, *Chem. Ber.*, 1964, **97**, 1193.

[23] J. S. Sörensen, T. Bruun, D. Holme, and N. A. Sörensen, *Acta Chem. Scand.*, 1954, **8**, 26.

methanol (21 ml.)–dichloromethane (6 ml.) was treated with 3% ozone–oxygen at −70° until a faint blue colour persisted. Excess of ozone was removed with nitrogen, and *trimethyl* phosphite [10] (1 ml.) was added to the cold solution. The mixture was kept first at −70° (1 hr.) and then at 10° (12 hr.); t.l.c. [ethyl acetate–light petroleum (1 : 1)] revealed the presence of four compounds [spots at R_F 0·6, 0·5, 0·33 (weak), and 0·17 (strong)]. These were obtained as the main components of four fractions by repeated chromatography on silica gel columns and 1 mm. layers and were postulated to be: (i) octa-2,4,6-triynal [24] (XIX), R_F 0·6, $\lambda_{max.}$ (ether) 337, 315, 295, 279, and 233 nm., $\nu_{max.}$ (CCl_4) 2200 and 2120 (C≡C) and 2700 and 1685 (CHO) cm.$^{-1}$; (ii) octa-2,4,6-triynal hemiacetal (XXI), R_F 0·5, $\lambda_{max.}$ (ether) 308, 283, 270, 255, and 240 nm., $\nu_{max.}$ (CCl_4) 3600 (OH), 2200 (C≡C), and 1070 and 1020 (COH and COMe) cm.$^{-1}$; (iii) 5,6-dihydro-4*H*-pyran-2-carbaldehyde (XXII), R_F 0·33, $\lambda_{max.}$ (ether) 254 nm., $\nu_{max.}$ (CCl_4) 1700 (CHO) and 1640 and 940 (CH=CH) cm.$^{-1}$; and (iv) 2-formyltetrahydropyran-3-yl acetate (XX), R_F 0·17, $[\alpha]_D$ *ca.* +11° (*c ca.* 0·5 in $CHCl_3$), $\nu_{max.}$ (CCl_4) 1740, 1370, 1230 and 1050 (OAc and CHO), and 1100 and 1085 (tetrahydropyran) cm.$^{-1}$. Fraction (iv) always gave rise in silica gel chromatography to the R_F 0·33 spot in addition to the R_F 0·17 spot originally present.

Synthesis of the Tetrahydropyranone (XVIII).—2,3-Dibromotetrahydropyran [prepared from dihydropyran (8·4 g.)] in ether was added with vigorous stirring and cooling to n-nonylmagnesium bromide [from n-nonyl bromide (20·7 g.) and magnesium (2·43 g.)] in ether at such a rate that the mixture was kept at −20°. The mixture was then allowed to warm gradually (3 hr.); it was decomposed with ice and aqueous ammonium chloride and extracted with ether. The extracts were concentrated and the residue (24 g.) was chromatographed on silica gel (250 g.). Light petroleum–ether (9 : 1) eluted the crude 3-*bromo*-2-*nonyltetrahydropyran* (XXIII) (9·8 g., 33%), b.p. 130—140° (block)/0·2 mm. [Found: C, 58·75; H, 9·65; Br. 26·7%; *M* (osmometer), 284. $C_{14}H_{27}BrO$ requires C, 57·3; H, 9·35; Br, 27·45%; *M*, 291], $\nu_{max.}$ (film) 1115 and 1090 (tetrahydropyran) and 712 (*eq* Br) cm.$^{-1}$.

A slurry of silver acetate (1·12 g.) in acetic acid (200 ml.) and acetic anhydride (20 ml.) was stirred under anhydrous conditions at 100—110° for 2 hr. Crude tetrahydropyranyl bromide (XXIII) (1·96 g.) was then added at 20°, and stirring was continued at 100—110° for 6 hr. The mixture was cooled, made alkaline with conc. aqueous potassium hydroxide, and extracted with ether. Concentration of the extracts gave a mixture of the tetrahydropyranyl and tetrahydrofurfuryl acetates as a mobile liquid (1·6 g., 88%), $\nu_{max.}$ (film) 1750, 1370, 1240 and 1040 (OAc), and 1100 and 1080 (CH·O·CH_2) cm.$^{-1}$, τ ($CDCl_3$) 5·49 (dt, *J* 9—10 and 4—4·5 Hz, C*H*OAc in tetrahydropyran) and 5·1 (q, *J* 5—6 Hz, C*H*OAc in tetrahydrofuran side chain) in a *ca.* 3 : 1 ratio.

The acetates (0·72 g.) were refluxed with 3% potassium hydroxide in aqueous methanol (1 hr.). The mixture was diluted with water and extracted with ether. Concentration of the extract yielded a mixture of the parent alcohols (0·6 g., 98%), $\nu_{max.}$ (film) 3450 (OH) and 1100 and 1075 (CH·O·CH_2) cm.$^{-1}$. This was oxidised with chromic acid in acetone and the ketones (0·52 g., 88%) thus obtained were converted into their 2,4-dinitrophenylhydrazones (0·59 g., 62%), which were separated by chromatography on silica gel (20 g.). Light petroleum–ether (9 : 1) eluted first the dinitrophenylhydrazone of 2-(n-decanoyl)tetrahydrofuran (XXV) (154 mg., 26%), m.p. and mixed m.p. 91—92° (see later). Further elution with the same solvent yielded (±)*tetrahydro*-2-(*n-nonyl*)*pyran*-3-*one* 2,4-*dinitrophenylhydrazone* (XXIV) (435 mg., 73%), m.p. 103—104° (Found: C, 59·0; H, 7·45; N, 12·75. $C_{20}H_{30}N_4O_5$ requires C, 59·1; H, 7·45; N, 13·8%). This (345 mg.) was refluxed with a laevulic acid (35 ml.)–chloroform (35 ml.)–hydrochloric acid (N; 3·5 ml.) mixture for 3 hr. The product was extracted with ether, and the extract was washed with sodium hydrogen carbonate solution and brine, dried, and concentrated. The residue was chromatographed on alumina (50 g.; deactived with 5% water); elution with light petroleum–ether (99 : 1) yielded the racemic ketone (XVIII) (116 mg., 60%), R_t value and i.r., n.m.r., and mass spectra identical with those recorded for the ketone (XVIII) obtained from the acetate (XIIIa).

Synthesis of 2-*Decanoyltetrahydrofuran.*—Furfuraldehyde (21 g.) and nonylmagnesium bromide [from n-nonyl bromide (54·2 g.) and magnesium (6·4 g.)] in ether gave a nearly quantitative yield of 1-(2-furyl)decan-1-ol, b.p. 106°/0·5 mm., n_D^{25} 1·4653 (lit.,[25] b.p. 144—145°/5 mm., n_D^{20} 1·4665), $\nu_{max.}$ (film) 3330 (OH) and 1510, 1010, 885, and 735 (furan) cm.$^{-1}$. This alcohol (7·5 g.) in ethanol (150 ml.) was hydrogenated over 5% palladium–charcoal (0·7 g.). The resulting oil was chromatographed on silica gel (200 g.) from ether–light petroleum and the fractions were monitored by g.l.c. (181°). Two major components were identified: 10—20% ether eluted 2-decyltetrahydrofuran (2·48 g.), b.p. 92—93°/0·6 mm., n_D^{20} 1·4441 (lit.,[26] b.p. 138°/12 mm., n_D^{20} 1·4498) (Found: C, 78·85; H, 13·3%; M^+, 212. Calc. for $C_{14}H_{28}O$ C, 79·2; H, 13·25%; *M*, 212), R_t 7·5 min., $\nu_{max.}$ (thin film) 1065 cm.$^{-1}$ (tetrahydrofuran); 70% ether eluted 1-(*tetrahydro-2-furyl*)*decan*-1-*ol* (3·1 g.), b.p. 110—111°/0·4 mm., n_D^{25} 1·4552 (Found: C, 73·3; H, 12·1%; M^+, 228. $C_{14}H_{28}O_2$ requires C, 73·6; H, 12·35%; *M*, 228), R_t 20 min., $\nu_{max.}$ (film) 3430 (OH) and 1065 (tetrahydrofuran) cm.$^{-1}$, τ (CCl_4) 9·12 (t, *J* 5 Hz, CH_3·[CH_2]-), 8·7br ([CH_2]$_n$), 8·16 (t, *J* 5 Hz, tetrahydrofuran β-H), 7·6 (s, OH), and 6·0—6·5 (m, CH_2·O·C*H* and C*H*·OH). The perhydro-alcohol (0·54 g.) in acetone was oxidised with chromic acid to 2-*decanoyltetrahydrofuran* (XXVI), b.p. 102—103°/0·5 mm., $\nu_{max.}$ (CCl_4) 1720 (CO) and 1075 (tetrahydrofuran) cm.$^{-1}$, τ (CCl_4) 9·10 (t, *J* 6 Hz, CH_3·CH_2), 8·7br ([CH_2]$_n$), 7·8—8·25 (m, tetrahydrofuran β-H), 7·48 (t, *J* 7 Hz, CH_2·CH_2·CO), 6·17 (t, *J* 6 Hz, O·CH_2·CH_2), and 5·48 [t, *J* 6 Hz, CH_2·(CO)C*H*·O], M^+ 226. The ketone formed the 2,4-*dinitrophenylhydrazone* (XXV), m.p. 91—92° (Found: C, 59·0; H, 7·35; N, 14·05. $C_{20}H_{30}N_4O_5$ requires C, 59·1; H, 7·45; N, 13·8%).

(2S,3R)-*Tetrahydro*-2-*hydroxymethylpyran*-3-*ol Bis*-3,5-*dinitrobenzoate* (XXVI) *from the Acetate* (XIIIa).—This (0·8 g.) in methanol (21 ml.) and dichloromethane (6 ml.) was treated with ozone as before. Excess of ozone was removed with nitrogen, sodium borohydride (0·4 g.) was added to the solution at −20°, and the mixture was kept at 20° until the reaction had ceased (*ca.* 1 hr.). The solvent was then evaporated off; the residue was dissolved in methanol–water (1 : 9) and shaken for 48 hr. with barium hydroxide (1 g.). The product was poured on solid carbon dioxide,

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[24] F. Bohlmann, W. von Kap-herr, C. Rybak, and J. Repplinger, *Chem. Ber.*, 1965, **98**, 1736.

[25] N. Tits-Skvortsova, A. A. Rybnikova, and N. N. Kushinova, *Zhur. obshchei Khim.*, 1960, **30**, 3316.

[26] B. Notari, A. Ferretti, and R. Onesta, *Gazzetta*, 1959, **89**, 1139.

warmed briefly to 60° and filtered. The filtrate was first extracted with light petroleum and then freed of methanol by concentration. The remaining aqueous solution was continuously extracted (24 hr.) with ether. The dried and concentrated ether extract and 3,5-dinitrobenzoyl chloride (1·5 g.) were dissolved in pyridine (5 ml.); the solution was kept at 40° for 1·5 hr. and then poured into 2N-hydrochloric acid; a precipitate formed and was taken up in benzene. The benzene solution was concentrated and the residue was chromatographed on 1 mm. layers by repeated development with dichloromethane. The band with the same R_F value as bisdinitrobenzoate (XXIX) was extracted with chloroform; the extract was filtered through a short pad of alumina and concentrated. The residue crystallised from acetone–light petroleum yielding needles of *bisdinitrobenzoate* (XXVI) (5 mg.), m.p. 166—168°, mixed m.p. with bisdinitrobenzoate (XXIX) 140—160°, $[\alpha]^{20}$ −52·5° (589 nm.), −56° 578 nm.), −63° (546 nm.), and −109·5° (436 nm.) (*c* 0·2 in $CHCl_3$; error ±2°); i.r. and mass spectra and R_F values in several solvent systems identical with those of bisdinitrobenzoate (XXIX).

(2R,3S)-*Tetrahydro*-2-*hydroxymethylpyran*-3-*ol* *Bis*-3,5-*dinitrobenzoate* (XXIX) *from* D-*Glucose*.—Triacetyl-D-glucal (10 g.), prepared from D-glucose as described by Wood *et al.*,[27] was converted by Fischer's method [18] into the crude, distilled (bath 160°/0·2 mm.) triacetyl-D-pseudoglucal (XXVII) (6·6 g.). This (1·2 g.) was hydrogenated with Adams catalyst in glacial acetic acid (palladium–charcoal in ethanol worked equally well; Bergmann [17] used palladium black) to crude 3-acetoxy-2-acetoxymethyltetrahydropyran (1·01 g.), which on hydrolysis with barium hydroxide gave crude tetrahydro-2-hydroxymethylpyran-3-ol (0·7 g.) (analysed by t.l.c. the product showed four spots). The thoroughly dried crude diol was converted into the benzylidene derivative (XXVIII) (0·3 g.), m.p. 125—140°, by the method of Foster and his co-workers; [28] it was recrystallised to constant rotation from acetone–water and light petroleum and melted at 139° (lit.,[17] 137—137·5°) (Found: C, 70·65; H, 7·2%; M^+, 220. Calc. for $C_{13}H_{16}O_3$: C, 70·9; H, 7·35%; *M*, 220), $[\alpha]^{20}$ −5° (589 nm.), −5·5° (578 nm.), −6° (546 nm.), −10° (436 nm.), and −16·5° (365 nm.) (*c* 1·0 in $CHCl_3$; error ±1°) (Bergmann [17] observed no rotation at 589 nm. with a 2% solution in tetrachloroethylene), $\nu_{max.}$ (CCl_4) 2950, 2850, 1380, 1140, 1100, 1020, and 980 cm.$^{-1}$, τ (CCl_4) 7·8—8·5 (m, $[CH_2]_2$), 5·7—6·9 (m, 6 × HC·O), 4·55 (s, PhC*H*O_2), and 2·6—2·8 (m, Ph). The benzylidene derivative (0·25 g.) was shaken (24 hr.) in sulphuric acid (0·5N; 10 ml.) and acetone (5 ml.). Partial concentration of the mixture was followed by extraction with light petroleum, addition of excess of barium hydroxide and then solid carbon dioxide to the aqueous solution, filtration, and concentration. The residual oil (single spot with R_F 0·5 in ether) was treated with 3,5-dinitrobenzoyl chloride in pyridine and worked up as already described. The benzene extract was chromatographed on 1 mm. layers (benzene–ether, 1 : 1) and the least polar fraction was recrystallised (acetone–light petroleum) yielding the *bisdinitrobenzoate* (XXIX) (0·15 g.), m.p. 168° (lit.,[16] 172°) (Found: C, 46·3; H, 3·1; N, 11·1. $C_{20}H_{16}N_4O_3$ requires C, 46·1; H, 3·1; N, 10·8%), $[\alpha]^{20}$ +50° (589 nm.), +55·5° (578 nm.), +62·5° (546 nm.), and +111° (436 nm.) (*c* 0·3 in $CHCl_3$; error ±2°), $\nu_{max.}$ ($CHCl_3$) 1730, 1630, 1550, 1470, 1350, 1280, and 1170 cm.$^{-1}$; *m/e* 520 (M^+), 308, 295, 195, 149, 113, 103, 96, 83, 75, and 71.

Hybrid

Isolation of the Polyacetylenes from the Roots.—The fresh tubers (950 g.) were extracted as described for the species. The concentrated ether solution was separated on silica gel (400 g.) by gradient elution chromatography [light petroleum–ether (9 : 1, 1·8 l.) was enriched with ether (1·8 l.) and subsequently ether (1 l.) was enriched with methanol (1 l.)]. Fractions (100 ml.) were collected and those of similar polarity and chromophore were combined and rechromatographed on silica gel and where necessary on alumina.

Fractions 1—3 showed only an ene-diyne-diene chromophore and gave all-*trans*-heptadeca-1,7,9,15-tetraene-11,13-diyne (VIII) (30 mg.), m.p. 29—30° (lit.,[29] 27—29°), u.v. and i.r. spectra identical with those reported; the perhydro-hydrocarbon (VIII) and n-heptadecane had identical R_t values.

Fractions 4 and 5 yielded traces of two polyacetylenes with ene-tetrayn-ene and ene-triyne-diene chromophores, belonging most likely to the hydrocarbons (I) and (III), and crystalline *trans*-phenylhept-5-ene-1,3-diyne (V) (250 mg.), m.p. and spectra identical with reported [30] values.

The final purification of fractions 11—15 was achieved on thin layers [light petroleum–ethyl acetate (7 : 3)] and yielded the non-crystalline *all*-trans-6-*acetoxyheptadeca*-1,7,9,15-*tetraene*-11,13-*diyne* (IX) (*ca.* 7 mg.), $\lambda_{max.}$ (ether) 336 (rel. *E* 0·75) 314 (1·0), 295 (0·73), 278 (0·43), 266 (0·76), and 251 (0·88) nm., $\nu_{max.}$ (CS_2) 3080, 1820, 915 (CH=CH_2), 1730, 1225 (OAc), 980 (*trans,trans*-CH=CH·CH=CH), and 945 (*trans*-CH=CH) cm.$^{-1}$. The acetate was hydrolysed with methanolic potassium hydroxide to the parent alcohol (XXX), which had u.v. and i.r. spectra identical with those of the synthetic compound (see later). The perhydro-alcohol (5% rhodium–charcoal) and n-heptadecan-6-ol had identical R_t values. The alcohol (XXX) and manganese dioxide in ether gave the unsaturated ketone (XXXI), m.p. 105—106°, mixed m.p. with the synthtic ketone 105—107°; the spectra were identical with those of the synthetic product. The perhydro-ketone and 6-oxoheptadecane had identical R_t values.

Fractions 19—22 yielded a fraction (*ca.* 1 mg.) with an ene-triyne-diene chromophore belonging to a compound which had the same R_F value as the acetate (IVa) and crystals, m.p. 75·5—76·5° (80 mg.) of (2S,3R)-*tetrahydro*-2-(*nona*-trans-1,trans-7-*diene*-3,5-*diynyl*)*pyran*-3-*yl* *acetate* (VIIa) [Found: *M* (osmometer), 258. $C_{16}H_{18}O_3$ requires *M*, 258], $[\alpha]_D^{22}$ +17° (*c* 0·5 in CCl_4), $\lambda_{max.}$ (EtOH) 312·5 (ε 20,000), 293·5 (24,500), 277 (16,500), 262 (9000), 248 (24,000), 237 (31,500), and 230 (31,000) nm., $\nu_{max.}$ (CCl_4) 2200, 2100 (C≡C), 1750, 1235, 1040 (OAc), 1105, 1085, 1070 (tetrahydropyran), 950, and 945 (*trans*-CH=CH) cm.$^{-1}$, $\nu_{max.}$ (CS_2) 1750, 1230, 1040, 1105, 1085, 1070, 950, and 945 cm.$^{-1}$, τ ($CDCl_3$) see Table 2. The hydrogenated (5% rhodium–charcoal) acetates (VIIa) and (XIIIa) had identical R_t values (12·8 min. at 180°). The acetate (VIIa) (35 mg.) was hydrolysed with methanolic potassium hydroxide (3%; 5 ml.) for 24 hr. at 20°. Isolation, chromatography, and crystallisation (ether–light petroleum) afforded stubby

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needles of the *alcohol* (VII) (20 mg.), m.p. 64—65° (Found: M^+, 216·1154. $C_{14}H_{16}O_2$ requires *M*, 216·1150), $\lambda_{max.}$ (EtOH) 312 (ε 20,000), 293·5 (25,000), 276 (16,500), 261 (8500), 247 (23,000), 237 (33,000), and 230 nm. (32,500), $\nu_{max.}$ ($CHCl_3$) 3600, 3420 (OH), 2200, 2130 (C≡C), 1100, 1085 (tetrahydropyran), 950, and 940 (*trans*-CH=CH) cm.$^{-1}$, τ ($CDCl_3$) 8·27 (s, OH), 8·15 (dd, *J* 7 and 1·5 Hz, C*H*$_3$·CH=CH), 7·7—8·6 (m, CH·C*H*$_2$·C*H*$_2$·CH_2·O), 5·8—6·8 (m, C*H*·OH and C*H*·O·C*H*$_2$), and 3·2—4·6 (m, CH_3·C*H*=C*H* and C*H*=C*H*·CHO), *m/e* 216 (M^+, 50%), 145 (50), 115 (80), 100 (85), and 71 (100) [the fragmentation pattern is analogous to that of the alcohol (XIII) interpreted elsewhere [9]]. The hydrogenated alcohol (VII) and the alcohol (XVII) had identical R_t values (13·8 min. at 184°).

Fractions 25—31 showed an ene-diyne chromophore and final purification on thin layers afforded the all-*trans*-diacetate (VI),[31] $\nu_{max.}$ (CS_2) 980 (*trans,trans*-CH=CH·CH=CH) and 945 (*trans*-CH=CH) cm.$^{-1}$.

Fractions 34—39 showed two chromophores and were further separated into two parts: a less polar fraction had an ene-diyn-ene chromophore (*ca.* 20 mg.) and a more polar fraction contained an ene-triyne-diene chromophore (*ca.* 3 mg.); neither could be purified sufficiently to crystallise. The former must be the alcohol (VII); $\lambda_{max.}$ and $\nu_{max.}$ values were identical with those found for the hydrolysis product of the acetate (VIIa) and the perhydro-compound had the same R_t value as the alcohol (XVII). The more polar part was the C_{13} alcohol (IV),[21] $\nu_{max.}$ ($CHCl_3$) 3600, 3450, 1090 (OH), 3080, 1830, 920 (CH=CH_2), 2180 (C≡C), 1620, 1580, 945 (*trans*-CH=CH), and 1000 (*trans*-CH=CH·CH=CH) cm.$^{-1}$. The hydrogenated alcohol (IV) and tetradecanol had identical R_t values (10·0 min. at 165°).

Isolation of the Polyacetylenes from the Leaves.—The concentrated ether extract from dried milled leaves (950 g.) was digested with light petroleum–ether (9 : 1) and the soluble part was separated on silica gel (300 g.) by gradient elution chromatography [light petroleum–ether (9 : 1; 1 l.) was enriched with ether (1 l.)] into fractions (100 ml.). The non-polar fractions showed triyne-diene absorption (corresponding to *ca.* 18 mg. of compound) and some phenyltriyne absorption (only traces of the compound could have been present). They were rechromatographed on columns and thin layers and the C_{17} hydrocarbon (XIV), u.v. and i.r. spectra identical with those described,[32] was isolated; the hydrogenated hydrocarbon and n-heptadecane had identical R_t values (13·8 min. at 156°). The more polar fractions contained traces of the acetate (XIIIa) and its parent alcohol (XIII).

Isolation of the Polyacetylenes from the Flowers.—The dried and milled flowers (110 g.) were extracted with ether and the extract was worked up and separated in the same way as the leaf extract. The C_{17} hydrocarbon (XIV) [32] (*ca.* 4 mg.) and traces of phenylheptatriyne (X) [33] appeared in fractions 1—4, the acetate (XIIIa) (*ca.* 10 mg.) in fractions 10 and 11, and the alcohol (XIII) (*ca.* 8 mg.) in fraction 14.

Synthesis of all-trans-*Heptadeca*-1,7,9,15-*tetraene*-11,13-*diyn*-6-*ol* (XXX).—*trans,trans*-7-Bromohepta-2,4-dien-6-yn-1-ol [34] (1·4 g.) in methanol (80 ml.) was added with stirring during 90 min. to *trans*-pent-2-en-4-yne [35] (2·0 g.), copper(I) chloride (0·24 g.), hydroxylamine hydrochloride (0·96 g.), dimethylformamide (36 ml.), and aqueous ethylamine (50%; 12 ml.) in methanol (200 ml.) at 20°. Stirring was continued for 24 hr. and solid potassium cyanide was then added; the mixture was diluted with an equal volume of saturated sodium chloride solution and extracted with ether. The extract was chromatographed and the fractions showing ene-diyne-diene absorption (*ca.* 600 mg.) were combined, concentrated, and crystallised from ether–light petroleum at −40° giving *all*-trans-*dodeca*-2,4,10-*triene*-6,8-*diyn*-1-*ol*, m.p. 126—127°, $\lambda_{max.}$ (EtOH) 335·5 (ε 26,000), 314 (35,000), 295·5 (25,500), 278·5 (14,000), 266 (25,500), and 250 (30,000) nm.; $\nu_{max.}$ (CS_2) 3600 (OH), 980 (*trans,trans*-CH=CH·CH=CH), and 945 (*trans*-CH=CH) cm.$^{-1}$, $\nu_{max.}$ ($CHCl_3$) 2190 and 2120 (C≡C) cm.$^{-1}$; τ ($CDCl_3$) 8·30 (s, OH), 8·16 (dd, *J* 7 and 1·5 Hz, C*H*$_3$·CH=CH), 5·72 (d, *J* 5·5 Hz, C*H*$_2$·OH), and 3—4·4 (m, C*H*=C*H* and C*H*=C*H*·C*H*=C*H*). The alcohol (250 mg.) was shaken with manganese dioxide (700 mg.) in ether (40 ml.) for 20 hr. at 20°. Chromatography and crystallisation (light petroleum) gave all-*trans*-dodeca-2,4,10-triene-6,8-diyn-1-al (210 mg.), m.p. 90—91° (lit.,[36] 88—89°); u.v. and i.r. spectra were identical with those published. The aldehyde (180 mg.) in tetrahydrofuran (40 ml.) was added dropwise during 30 min. to pent-4-enylmagnesium bromide [prepared from 1-bromopent-4-ene (765 mg.) and magnesium turnings (130 mg.)] in tetrahydrofuran (10 ml.) with stirring under nitrogen. The usual work-up resulted in an ether extract which was chromatographed on silica gel. The fractions showing ene-diyne-diene absorption (65 mg.) were rechromatographed on alumina and yielded very unstable crystals (ether–light petroleum) of *all*-trans-*heptadeca*-1,7,9,15-*tetraene*-11,13-*diyn*-6-*ol* (XXX), m.p. 41—42°, $\lambda_{max.}$ (EtOH) 336 (ε 27,000), 314 (37,000), 295·5 (26,500), 278 (15,500) 266·5 (27,500), and 251 (31,500) nm., $\nu_{max.}$ (CS_2) 3600 (OH), 3075, 1825, 910 (CH=CH_2), 980 (*trans,trans*-CH=CH·CH=CH), and 945 (*trans*-CH=CH) cm.$^{-1}$, $\nu_{max.}$ ($CHCl_3$) 2195, 2120 (C≡C), 1640, 1580, and 945 (*trans*-CH=CH) cm.$^{-1}$, τ ($CDCl_3$) 8·4—8·6 (m, CH_2·C*H*$_2$·CH_2), 8·32 (s, OH), 8·15 (dd, *J* 7 and 1·5 Hz, C*H*$_3$·CH=CH), 7·8—8·1 (m, C*H*$_2$·CH_2·C*H*$_2$·CH=CH_2), 5·79 (q, *J* 5·5 Hz, C*H*·OH), 4·8—5·2 (m, C*H*=C*H*$_2$), and 3·0—4·6 (m, C*H*=C*H* and C*H*=C*H*·C*H*=C*H*). The alcohol (XXX) (12 mg.) and excess of manganese dioxide were shaken in ether (5 ml.) for 24 hr. at 20°. Filtration and chromatography on neutral alumina (10 g.) gave a quantitative yield of *all*-trans-*heptadeca*-1,7,9,15-*tetraene*-11,13-*diyn*-6-*one* (XXXI), m.p. 106—107° (light petroleum) (Found: C, 85·5; H, 8·0. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%), $\lambda_{max.}$ (EtOH) 354sh (ε 24,000), 339 (29,000), 322sh (25,000), 306 (10,000), 275 (17,500), and 264 (18,000) nm., $\nu_{max.}$ (CS_2) 3080, 1820, 910 (CH=CH_2), 1695, 1670 (CH=CH·CO), 985 (*trans,trans*-CH=CH·CH=CH), and 945 (*trans*-CH=CH) cm.$^{-1}$, $\nu_{max.}$ ($CHCl_3$) 2190 (C≡C) cm.$^{-1}$.

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