Natural Acetylenes. Part XXXVI.[1] Polyacetylenes from the Lobeliaceae Plant Family. A C_{14} Enediyne Triol from *Lobelia cardinalis* L.[2]

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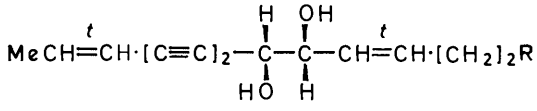
The isolation and determination of structure and absolute stereochemistry of the new triol MeCH=CH·[C≡C]$_2$·CH(OH)·CH(OH)·CH=CH·[CH$_2$]$_2$·CH$_2$·OH from *Lobelia cardinalis* L. and the hybrid *Lobelia x vedariensis* are described. The corresponding dihydroxy-aldehyde structure is suggested for a minor polyacetylene from the hybrid.

THE detection of polyacetylenes in *Lobelia* species has been reported recently.[3] Further screening indicates that the occurrence of polyacetylenes in the Lobeliaceae family, as in the taxonomically close Campanulaceae, could be widespread. We now describe the investigation of *L. cardinalis* L. and the hybrid *L. x vedariensis*.† The aerial parts of the former were richer in polyacetylenes than the roots (50 and 5 mg per kg fresh plant material, respectively, roughly estimated from the u.v. spectra of the extracts) whilst in the hybrid the polyacetylenes were more abundant in the roots (20 and 70 mg per kg, respectively). Although several polyacetylenes were detected in the extracts of the two specimens, only the major constituent, common to both species and hybrid, the new enediynetriol (I), was completely identified. In addition, one of the minor constituents of the hybrid is probably the dihydroxy-aldehyde (II).



(I) R = CH$_2$·OH (II) R = CHO

The chemical transformations in Scheme 1 were used in the structure determination of the triol (I). The enediynediol part of the structure followed from the

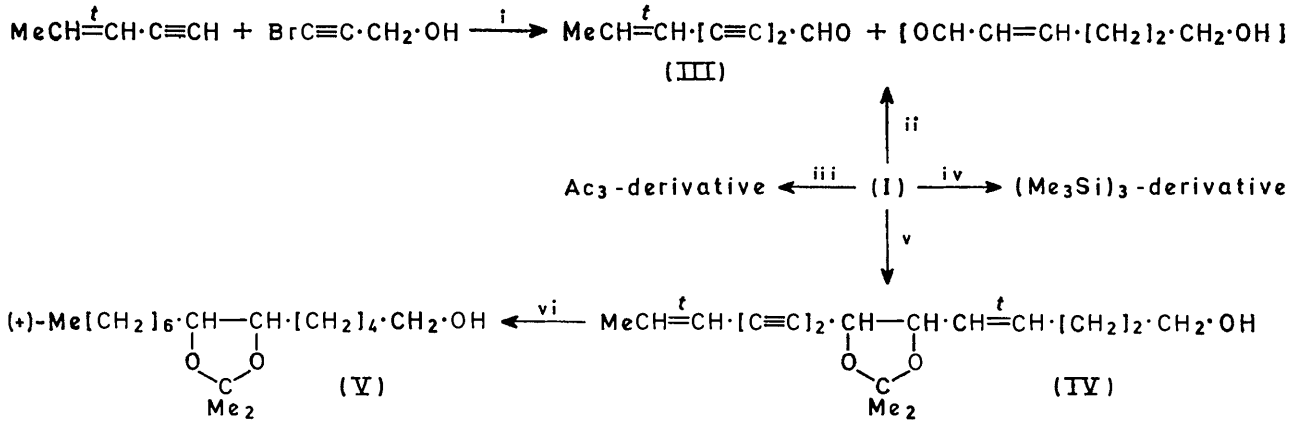
† According to the Royal Horticultural Society this is most probably a hybrid of *L. cardinalis* and *L. syphilitica*.

[1] Part XXXV, V. Thaller and J. L. Turner, *J.C.S. Perkin I*, 1972, 2032.

[2] A more detailed account of part of the work described in this paper is in the D.Phil. Thesis of R. A. M. Ross, Oxford, 1970.

[3] R. K. Bentley, J. K. Jenkins, Sir Ewart R. H. Jones, and V. Thaller, *J. Chem. Soc.* (*C*), 1969, 830.

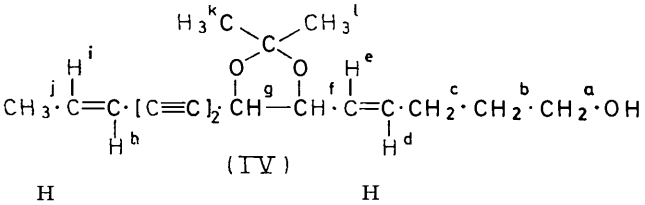
u.v. spectra of the triol and its periodate fission product and the n.m.r. spectrum of the triol. The molecular formula was deduced from the molecular ions, recognisable in the mass spectra of the acetyl and trimethylsilyl derivatives, and the position of the isolated double bond was evident from the n.m.r. spectrum of the isopropylidene derivative (IV) (Table 1). The triol (I) suffered a fragmentation analogous to cleavage by periodate in the mass spectrometer, and the corresponding fragments appeared as major peaks (Scheme 2). The intense peak at *m/e* 120 could be due to a ready fragmentation through intramolecular hydrogen abstraction from the saturated half of the triol molecule.



SCHEME 1 Reagents: i, CuCl–NH_2·OH–$EtNH_2$, MnO_2; ii, $NaIO_4$; iii, Ac_2O–C_5H_5N; iv, Me_3SiCl–$(Me_3Si)_2NH$–C_5H_5N; v, Me_2CO–$CuSO_4$–TsOH; vi, Pd–EtOAc, Pt–Et_2O

TABLE 1

Chemical shifts (τ) and coupling constants (J/Hz) for the isopropylidene derivative (IV) in $(CD_3)_2SO$ (100 MHz)

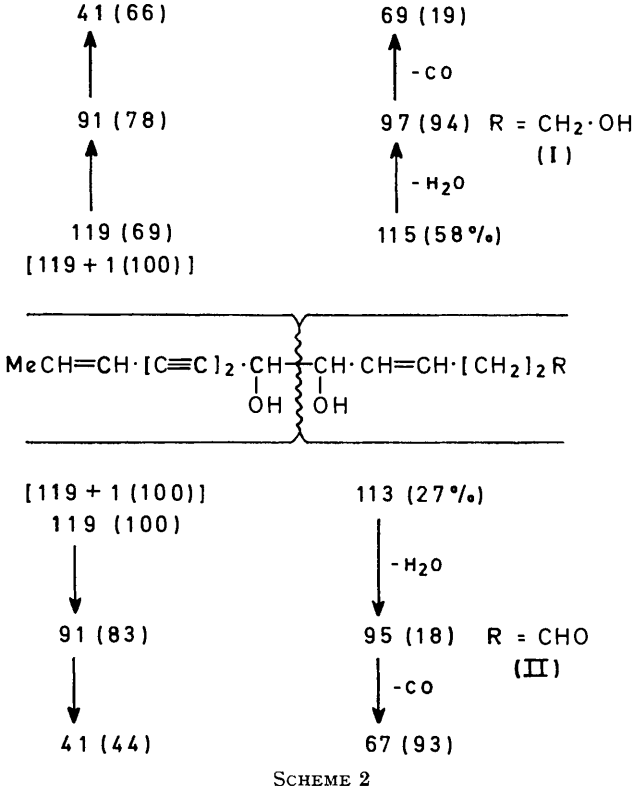


(IV)

H		H	
a;	6·61 (t, 6·5)	h;	4·34 (dq, 16 and 1·5)
b;	8·47 (m)	i;	3·54 (dq, 16 and 6·5)
c;	7·94 (dt, 7)	j;	8·21 (dd, 6·5 and 1·5)
d;	4·12 (dt, 16 and 7)	k;	8·66 (s)
e;	4·6 (dd, 16 and 7)	l;	8·63 (s)
f; g;	5·55 (m, AB system)		

Assignment of the absolute configuration of the triol (I) as (6*R*,7*R*) followed from the absolute configuration of the dioxolan (V). The optical rotation of the latter was very similar to those of long chain *threo*-glycols (Table 2) and its *threo*-configuration was confirmed by direct g.l.c. comparison with the isopropylidene derivatives of racemic *threo*- and *erythro*-tetradecane-1,6,7-triols, synthesised for this purpose (Scheme 3). It is known that rotations of long chain *threo*-glycols do not change significantly as a consequence of either chemical transformations of groups distant from the asymmetric centres or conversion of the glycol into the corresponding dioxolan (for examples see Table 2). Thus the dioxolan (V) must have the same absolute configuration as (6*R*,7*R*)-pentadecane-6,7-diol.[4]

Material from the hybrid root extract, exhibiting an enediyne band which ran on the chromatogram just in front of the triol (I), showed carbonyl absorption in the i.r. and a fragmentation pattern in the mass spectrum (Scheme 2) similar to that of the triol (I). The fragments from the saturated half of the molecule have



SCHEME 2

[4] T. Irie, M. Izawa, and E. Kurosawa, *Tetrahedron*, 1970, **26**, 851.

TABLE 2

Molecular rotations of long-chain *threo*-diols

		$[M]_D$
	$Me[CH_2]_6\cdot CH(O)CH\cdot[CH_2]_4\cdot CH_2\cdot OH$ (V)	+ 71
threo-	$Me[CH_2]_7\cdot CH(OH)CH\cdot[CH_2]_7\cdot CO_2H$	+ 74[a]
	$CH_2\cdot OH$	+ 77[a]
threo-	$Me[CH_2]_5\cdot CH(OH)CH\cdot[CH_2]_7\cdot CO_2H$	− 64[b]
	$CH(O)CH$	− 88[b]
	(6*R*,7*R*)-$Me[CH_2]_7\cdot CH(OH)CH\cdot[CH_2]_4Me$	+ 62[c]

[a] J. F. McGhie, W. A. Ross, and D. J. Polton, *Chem. and Ind.*, 1956, 353. [b] D. F. Ewing and C. Y. Hopkins, *Canad. J. Chem.*, 1967, **35**, 1259. [c] Ref. 4.

two mass numbers less and relative intensities which point to an easy loss of carbon monoxide during the fragmentation, as for the dihydroxy-aldehyde (II). As expected the sodium borohydride reduction product and the triol (I) showed identical t.l.c. behaviour, but lack of material prevented complete characterisation.

EXPERIMENTAL

Equipment: u.v. (in Et_2O unless stated otherwise), Unicam SP 800; i.r., Perkin-Elmer 237 and 257; n.m.r., Perkin-Elmer R10 and R14; mass spectra (direct insertion), A.E.I. MS9 and Atlas CH7; specific rotations, Perkin-Elmer 141; m.p. (corr.) Kofler hot-stage apparatus.

Liquid chromatography: SiO_2 Whatman SG31 and Merck G in columns and Merck $HF_{254+366}$ and $PF_{254+366}$ in 0·3 (t.l.c.) and 1 mm (p.l.c.) layers, respectively. $AgNO_3$-impregnated SiO_2 plates for argentation chromatography were prepared from $PF_{254+366}$ and aqueous 10% $AgNO_3$ instead of H_2O. The layers were dried for 12 h at 20° and activated before use at 110° for 5 min.

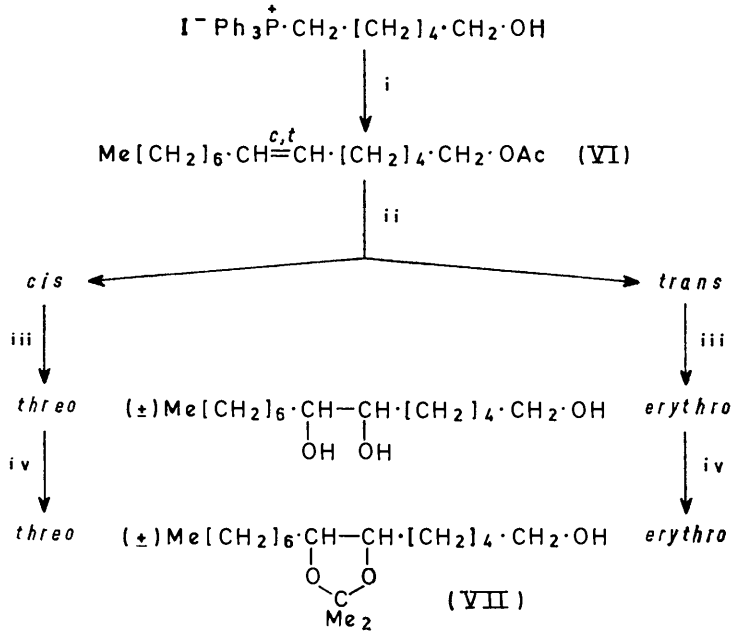
G.l.c.: 10% poly(ethylene glycol succinate) on Embacel (60—100 mesh) in a 5 ft column and a Pye 104 series model 24 instrument, argon flow rate 40 ml min^{-1}.

Petrol refers to light petroleum, b.p. 30—40°. All reactions were carried out under nitrogen and protected from light.

Screening of Lobelia *Species*.—Polyacetylenic chromophores have now also been detected in extracts of *L. anceps* Thunb. and *L. syphilitica* L.

General Procedure for Isolation of Polyacetylenes.—The chopped roots or aerial parts of plants harvested at the termination of flowering were extracted twice with Et_2O (24 h; 20°), the extract was dried and concentrated, and the residue was chromatographed [SiO_2 column (200 g)] by gradient elution [CH_2Cl_2 (500 ml) was enriched first with Et_2O (750 ml) and then with Et_2O–MeOH (9 : 1; 500—1000 ml)]. Fractions (50 ml) were assayed spectrophotometrically and those with similar properties were combined and rechromatographed, first on dry packed SiO_2 G columns with Et_2O–MeOH (3 : 1), and then on SiO_2 layers with several solvent systems [Et_2O, Et_2O–MeOH (various proportions), and $CHCl_3$–MeOH (9 : 1)].

Polyacetylenes of Lobelia cardinalis *L.* '*Queen Victoria*'.—(*a*) The extract from the roots (750 g) showed polyacetylene absorption, $\lambda_{max.}$ 280, 266, and 253 nm (estimated *ca.* 2 mg),



SCHEME 3 Reagents: i, Bu^n-Li–$Me[CH_2]_6$·CHO, Ac_2O–C_5H_5N; ii, SiO_2–$AgNO_3$ chromatography; iii, $MeCO_3H$, KOH–MeOH; iv, Me_2CO–H^+

in only one set of medium-polarity fractions together with *ca.* 1 g of non-acetylenic material and was not further investigated.

(*b*) The extract from the aerial parts (400 g) showed polyacetylene absorption in two sets of polar fractions. The less polar of the two yielded the liquid (6R,7R)-trans,-trans-*tetradeca*-4,12-*diene*-8,10-*diyne*-1,6,7-*triol* (I) (18 mg), $[\alpha]^{20}$ +33° (589 nm), +35° (578), +40° (546), +71° (436), and +194° (365) (*c* 0·745 in EtOH), $\lambda_{max.}$ (MeOH) 284 (ε 8400), 268 (11,400), 254 (8200), 241 (4300), and 215 (36,000) nm, $\nu_{max.}$ ($CHCl_3$) 3375 (OH), 2230 (C≡C), 1630, 970, and 950 (*trans*-CH=CH) cm^{-1}, τ ($CDCl_3$–D_2O) 8·34 (m, CH_2·CH_2·CH_2·OH), 8·16 (dd, *J* 6·5 and 1·5 Hz, CH_3·CH=CH), 7·84 (dt, *J* 7 Hz, CH=CH·CH_2·CH_2), 6·33 (t, *J* 7 Hz, CH_2·CH_2·OH), 5·8 [m, AB system, C≡C·CH(OH)·CH(OH)·CH=CH], 4·4 (m, CH=CH·C≡C and CH(OH)·CH=CH), 4·1 (dt, *J* 16 and 7 Hz, *trans*-CH=CH·CH_2), and 3·62 (dq, *J* 16 and 6·5 Hz, CH_3·CH=CH); for mass spectrum see Scheme 2, and a trace of a polyacetylene with $\lambda_{max.}$ 320, 303, 283, 268, and 251 nm. The more polar fraction contained 3—4 mg of a dienediyne, $\lambda_{max.}$ 301, 283, and 268 nm, which decomposed during attempted acetylation.

Polyacetylenes of Lobelia x vedariensis.—(*a*) The extract from the roots (1 kg; the plants were harvested after flowering) showed weak absorption, $\lambda_{max.}$ 279, 264, and 251 nm, in fractions 1—3 from the column in which only traces of polyacetylenes were present. The combined fractions 13—22 with $\lambda_{max.}$ 300w, 284, 268, and 253 nm were rechromatographed on 1 mm layers (Et_2O–MeOH, 97 : 3) and gave a major band (R_F 0·2) from which the triol (I) (65 mg) was isolated. The extract from a minor, less polar band (R_F 0·35) was rechromatographed with Et_2O (2 developments; R_F 0·45) and $CHCl_3$–MeOH (19 : 1) (R_F 0·3); the purified material (5 mg), possibly the aldehyde (II), had $\lambda_{max.}$ 283 (rel. *E* 0·8), 268 (1·0), 253 (0·7), and 240 nm (0·35), $\nu_{max.}$ ($CHCl_3$) 1725 cm^{-1}; for mass spectrum see Scheme 2. On $NaBH_4$ reduction, the u.v. absorption remained unchanged, but the mobility of the single spot given by the reduced product in t.l.c. (Et_2O–MeOH, 99 : 1) became the same as that of the triol (I).

(*b*) From the aerial parts (1 kg) only the triol (I) (20 mg) was isolated.

Triol (I) *Triacetate.*—Triol (5 mg), Ac_2O (1 ml), and pyridine (1 drop) were mixed at 0°, then kept for 12 h at 20°. Usual work-up and p.l.c. (petrol–Et_2O, 1 : 1) gave the liquid *triol* (I) *triacetate* (3 mg), $\lambda_{max.}$ 283 (ε 8200), 267 (11,100), 253 (8200), 240 (4400), and 215 nm (30,000), $\nu_{max.}$ ($CHCl_3$) 3020, 1630, 960, 950 (conjugated and non-conjugated *trans*-CH=CH–), 2240 (C≡C), and 1735 cm^{-1} (acetate), *m/e* 360 (M^+, 4%), 318 (4), 301 (18), 276 (8), 258 (17), 199 (12), 162 (32), 157 (16), 139 (35), 102 (10), and 97 (100).

Triol (I) *Tristrimethylsilyl Ether.*—Triol (5 mg) in pyridine (5 drops) was treated with $(Me_3Si)_2NH$ (2 drops), and Me_3SiCl (1 drop). Concentration at 20° in vacuum and t.l.c. yielded the *triol* (I) *tristrimethylsilyl ether*, $\lambda_{max.}$ 283 (rel. *E* 1·0), 267 (1·4), and 253 nm (1·0), $\nu_{max.}$ ($CHCl_3$) 3030, 1670, 1630, 965, and 930 (conj. and non-conj. *trans*-CH=CH), 2230 (C≡C), 1250 and 1100 (SiOMe) cm^{-1}, *m/e* 450 (M^+, 2%), 435 (2), 360 (1), 271 (1), 259 (97), 191 (21), 169 (100), 147 (21), and 103 (17) [*m** 204 (450 ⟶ 271) and 110·3 (259 ⟶ 169)].

(4R,5R)-4-(*Hept*-trans-5-*ene*-1,3-*diynyl*)-5-(5-*hydroxypent*-trans-1-*enyl*)-2,2-*dimethyl*-1,3-*dioxolan* (IV).—Triol (I) (20 mg), anh. $CuSO_4$ (500 mg), and TsOH (2 mg) were shaken in Me_2CO (20 ml) for 12 h in N_2 in dark. K_2CO_3 (10 mg) addition, filtration, and t.l.c. (petrol–ether, 1 : 1; 2 runs) of the concentrated filtrate yielded the *dioxolan* (IV) (20 mg, 85%; R_F 0·7), b.p. 130—140° (block) at 0·005 mmHg; the distillate was an amorphous solid, m.p. 25—27°, $[\alpha]^{20}$ +139° (589 nm), +145° (578), +166° (546), +302° (436), and +534° (365) (*c* 0·79 in EtOH), $\lambda_{max.}$ 286 (ε 8600), 270 (14,200), 255 (10,000), 243 (5100), 216 (47,000), and 209 nm (39,000), $\nu_{max.}$ (CCl_4) 3620, 1040 (OH), 2240 (C≡C), 960, 935, 910 (conjugated and unconjugated *trans*-CH=CH), 1385 and 1375 (CMe_2) cm^{-1}, *m/e* 274 (M^+, 0·4%), 160 (36), and 102 (100); for n.m.r. see Table 1. The *p*-phenylazobenzoyl ester failed to crystallise (hexane and CCl_4, −20°).

(4R,5R)-4-*Heptyl*-5-(5-*hydroxypentyl*)-2,2-*dimethyl*-1,3-*dioxolan* (V).—Dioxolan (IV) (17 mg) in EtOAc was hydrogenated over 5% Pd–$CaCO_3$ for 8 h and then over PtO_2 (5 mg) in Et_2O (70 ml) for 48 h. P.l.c. (petrol–Et_2O, 1 : 1) yielded the liquid *dioxolan* (V) (3·5 mg, 17%; R_F 0·4), $[\alpha]^{20}$ +25° (589 nm), +28·5° (578), +31° (546), +48° (436), and +67° (365) (*c* 0·17 in EtOH), no $\lambda_{max.}$ >210 nm, $\nu_{max.}$ 3600 (OH), 1385 and 1375 cm^{-1} (CMe_2), t_R (160°) 24 min (identical, by co-chromatography, with the synthetic racemic *threo*-acetonide; see later), *m/e* 271 (M^+ −15; 100%), 211 (10), 59 (90), and 43 (95).

Periodate Cleavage of the Triol (I).—Triol (I) (20 mg) and $NaIO_4$ (200 mg) in H_2O (25 ml) were shaken (20°; 2 h). Extraction with ether and t.l.c. of the extract yielded oct-*trans*-6-ene-2,4-diynal (III), identical with a synthetic specimen. The aqueous solutions were evaporated to dryness, and the residue was extracted with $CHCl_3$. The extract had $\nu_{max.}$ ($CHCl_3$) 1700 cm^{-1} but 6-hydroxyhex-2-enal could not be isolated and characterised; however, hex-2-ene-1,6-diol [5] and MnO_2 in CH_2Cl_2 gave a product with similar carbonyl absorption and t.l.c. behaviour.

Oct-trans-6-*ene*-2,4-*diynal* (III).—Crude oct-*trans*-6-ene-2,4-diyn-1-ol [prepared from 3-bromoprop-2-yn-1-ol (200 mg, 1·5 mmol) and *trans*-pent-3-en-1-yne (100 mg, 1·5 mmol) by Chodkiewicz coupling], $\lambda_{max.}$ 283, 267, and 253 nm, was shaken with MnO_2 (800 mg) in CH_2Cl_2 (50 ml) for 5 h. Work-up and chromatography afforded the aldehyde (III) [6] (45 mg, 25%), $\lambda_{max.}$ 318 (ε 8000), 300 (8500), 284 (7000), 269 (5500), 253 (4000), 235 (23,000), and 228 nm (12,000), $\nu_{max.}$ ($CHCl_3$) 2700, 1660 (CHO), 2200, 2115 (C≡C), and 950 cm^{-1} (*trans*-CH=CH), τ (CCl_4) 8·07 (dd, *J* 6·5 and 1·5 Hz, CH_3·CH=CH), 4·38 (dq, *J* 16 and 1·5 Hz, CH_3·CH=CH), 3·5 (dq, *J* 16 and 7 Hz, CH_3·CH=CH), and 0·75 (s, CHO).

cis- *and* trans-*Tetradec*-6-*enyl Acetate* [cis- *and* trans- (VI)]. Bu^n-Li (15% hexane solution; 19 mmol) was added slowly to a stirred suspension of 6-hydroxyhexyltriphenylphosphonium iodide [7] (4·9 g, 10 mmol; m.p. 131—132°) in dry tetrahydrofuran (150 ml) under N_2 until a clear red solution was formed. To this, octanal (1·1 g, 8·6 mmol) was introduced during 0·5 h until the colouration just disappeared. After 2 h addition of saturated NH_4Cl (75 ml), isolation with Et_2O and p.l.c. (petrol–Et_2O, 1 : 1) afforded the oily tetradec-6-en-1-ol (1·4 g, 77%), t_R (140°) 11·0 min (one peak), which appeared homogeneous on SiO_2 but was resolved into two spots on argentation t.l.c.

This alcohol (1·2 g, 5·7 mmol) was added dropwise to stirred pyridine (10 ml) and Ac_2O (10 ml) at 0°. After 48 h at 20° isolation with Et_2O and p.l.c. (petrol–ether, 10 : 1; four runs) gave a main zone (R_F 0·8) which on extraction

[5] E. Takagi and I. Tosaka, Jap. P. 308/1957 (*Chem. Abs.*, 1958, **52**, 2894g).

[6] F. Bohlmann and H. Sinn, *Chem. Ber.*, 1955, **88**, 1869.

[7] D. Bhattacharjee, D.Phil. Thesis, Oxford, 1968.

yielded liquid *cis*- and *trans*-tetradec-6-enyl acetate (VI) (1·2 g, 83%), t_R (160°) single peak at 5·3 min, $\nu_{max.}$ (thin film) 1735, 1220, 1020 (acetate), 965 (*trans*-CH=CH), and 720 cm^{-1} (*cis*-CH=CH), τ (CCl_4) 9·1 (t, *J* 7 Hz, $CH_3{\cdot}CH_2$), 8·7br ($CH_3{\cdot}[CH_2]_5$ and $[CH_2]_3{\cdot}CH_2O$), 8·0 (m, $CH_2{\cdot}CH{=}CH{\cdot}CH_2$ with superimposed singlet $CH_3{\cdot}CO$), 6·01 (t, *J* 6·5 Hz, $CH_2{\cdot}OAc$), and 4·7 (m, CH=CH).

This mixture (600 mg) was resolved by argentation p.l.c. (petrol–Et_2O, 25 : 1; multiple development). The less polar (R_F 0·7) trans-*tetradec-6-enyl acetate* [*trans*-(VI)] (150 mg, 25%) distilled at 160—165° (block) and 3 mmHg; n_D^{20} 1·4462, $\nu_{max.}$ (CCl_4) 965 cm^{-1} (*trans*-CH=CH), τ (CCl_4) 4·62 (CH=CH; $W_{\frac{1}{2}}$ 8 Hz, comparable to the corresponding signal of elaidate).

The more polar (R_F 0·3) cis-*tetradec-6-enyl acetate* [*cis*-(VI)] (420 mg, 70%) distilled at 170—175° (block) and 3 mmHg; n_D^{20} 1·4478 (Found: C, 75·8; H, 12·0. $C_{16}H_{30}O_2$ requires C, 75·8; H, 11·9%), $\nu_{max.}$ (film) 720 cm^{-1} (*cis*-CH=CH), τ 4·62 (CH=CH, $W_{\frac{1}{2}}$ 12 Hz, comparable to the corresponding signal of oleate).

(±)-(*mainly*)threo-4-*Heptyl*-5-(5-*hydroxypentyl*)-2,2-*dimethyl*-1,3-*dioxolan* [threo-(VII)].—The foregoing unresolved *cis–trans* (3 : 1) acetate (180 mg) was shaken with AcO_2H (1 ml; 40% w/v) in $CHCl_3$ (10 ml) for 48 h. After basification, the products were isolated with Et_2O and separated by t.l.c. (petrol–Et_2O, 1 : 1; continuous development) into 4 components: (i) *trans*-6,7-epoxytetradecanyl acetate (34 mg; R_F 0·95, single elution), $\nu_{max.}$ (film) 1735, 1240, 1040 (acetate), and 900 cm^{-1} (*trans*-epoxide), τ (CCl_4) 9·1 (t, *J* 7 Hz, $CH_3{\cdot}CH_2$), 8·6br ($[CH_2]_6{\cdot}$  $[CH_2]_4$), 8·03 (s, $CH_3{\cdot}CO$), 7·53 (m, *trans*-$CH_2{\cdot}$  CH_2), and 6·0 (t, *J* 6·5 Hz, $CH_2{\cdot}CH_2{\cdot}OAc$); (ii) *cis*-6,7-epoxytetradecanyl acetate (17 mg; R_F 0·9, single elution), $\nu_{max.}$ (film) 1735, 1240, 1040 (acetate), and 840 cm^{-1} (*cis*-epoxide), τ (CCl_4) 9·1, 8·6br, 8·03, and 6·0 (all as above), and 7·3 (m, *cis*-$CH_2{\cdot}$  CH_2); (iii) (mainly) *threo*-7(or 6)-hydroxytetradecane-1,6(or 7)-diyl diacetate (80 mg; R_F 0·65, three elutions), $\nu_{max.}$ (CCl_4) 3600w (OH) and 1735 cm^{-1} (acetate), τ (CCl_4) 9·1 (t, *J* 7 Hz, $CH_3{\cdot}CH_2$), 8·6br ($Me[CH_2]_6$ and $[CH_2]_4{\cdot}CH_2{\cdot}OAc$), 8·03 (s, $CH_2{\cdot}O_2C{\cdot}CH_3$), 7·98 (s, $CH{\cdot}O_2C{\cdot}CH_3$), 6·5 (m, CH·OH), 5·98 (t, *J* 6·5 Hz, $CH_2{\cdot}OAc$), and 5·25 (m, CH·OAc); (iv) (mainly) *threo*-6,7-dihydroxytetradecanyl acetate (100 mg; R_F 0·3, three elutions), $\nu_{max.}$ 3600, 3580 (OH), 1735, 1235, and 1040 cm^{-1} (acetate), τ (CCl_4) 9·1 (t, *J* 7 Hz, $CH_3{\cdot}CH_2$), 8·6br $\{[CH_2]_6{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_4\}$, 8·03 (s, $CH_3{\cdot}CO$), 6·5 [m, $CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2$], and 5·98 (t, *J* 6·5, $CH_2{\cdot}CH_2{\cdot}OAc$).

The combined (mainly) *threo*-hydroxy-acetates (iii) and (iv) (180 mg) and KOH (2 g) in MeOH (25 ml) were kept for 24 h at 40°. Et_2O isolation yielded (±)(mainly)*threo*-tetradecane-1,6,7-triol (105 mg), an amorphous solid, $\nu_{max.}$ ($CHCl_3$) 3600 cm^{-1} (OH), τ ($CDCl_3$) 9·1 (t, *J* 7 Hz, $CH_3{\cdot}CH_2$), 8·6br ($CH_3{\cdot}[CH_2]_6$ and $[CH_2]_4{\cdot}CH_2{\cdot}OH$), 8·0br (s, disappears on addition of D_2O, OH), 6·56 [m, $CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2$], and 6·34 (t, *J* 6·5 Hz, $CH_2{\cdot}CH_2{\cdot}OH$).

The triol (100 mg) and anh. $CuSO_4$ (1 g) were shaken in dry Me_2CO (10 ml) for 10 h. Et_2O isolation and p.l.c. (petrol–Et_2O, 1 : 1) yielded a single band (R_F 0·3) of (±)-(mainly)threo-4-*heptyl*-5-(5-*hydroxypentyl*)-2,2-*dimethyl*-1,3-*dioxolan* (100 mg), b.p. 125—145° (block) at 0·05 mmHg, n_D^{20} 1·4539 (Found: C, 71·1; H, 12·2. $C_{17}H_{34}O_3$ requires C, 71·3; H, 11·95%), $\nu_{max.}$ (CCl_4) 3600 (OH), 1375, 1365 (CMe_2), 1170, 1100, and 1050 cm^{-1} (C–O), τ 9·1 (t, *J* 7 Hz, $CH_3{\cdot}CH_2$), 8·7br ($Me[CH_2]_6$ and $[CH_2]_4{\cdot}CH_2{\cdot}OH$), 8·7 (s, $CH_3{\cdot}C{\cdot}CH_3$), and 6·4 (t, *J* 6·5 Hz, $CH_2{\cdot}CH_2{\cdot}OH$, and m, $CH_2{\cdot}CH(O{-}){\cdot}CH(O{-}){\cdot}CH_2$), t_R (160°) 24 (70%, *threo*) and 32 min (30%, *erythro*), *m/e* 271 ($M^+ - 15$, 95%), 211 (9), 59 (100), 43 (95).

(±)-erythro-4-*Heptyl*-5-(5-*hydroxypentyl*)-2,2-*dimethyl*-1,3-*dioxolan*[erythro-(VII)].—*trans*-Tetradec-6-enyl acetate [*trans*-(VII)] (25 mg) was treated with AcO_2H as before and afforded on alkaline hydrolysis the liquid (±)-*erythro*-tetradecane-1,6,7-triol. This was converted into (±)-erythro-4-*heptyl*-5-(5-*hydroxypentyl*)-2,2-*dimethyl*-1,3-*dioxolan* [*erythro*-(VII)] (16 mg, 57%) which distilled at 150—170° (block) and 0·05 mmHg, n_D^{23} 1·4550 (Found: C, 71·55; H, 11·7. $C_{17}H_{34}O_3$ requires C, 71·3; H, 11·95%), i.r. spectrum identical with that of the *threo*-isomer save in relative intensities of the 1050 cm^{-1} peak, τ (CCl_4) 9·1 (t, *J* 7 Hz, $CH_3{\cdot}CH_2$), 8·6br ($CH_3{\cdot}[CH_2]_6$ and $[CH_2]_4{\cdot}CH_2{\cdot}OH$, with superimposed singlets at τ 8·66 and 8·76, CMe_2), 6·43 (t, *J* 6·5 Hz, $CH_2{\cdot}CH_2{\cdot}OH$), and 6·05 [m, $CH_2{\cdot}CH(O{-}){\cdot}CH(O{-}){\cdot}CH_2$], t_R (160°) 32 min (single peak), *m/e* 271 ($M^+ - 15$, 100%), 211 (20), 59 (94), and 53 (95).

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