Natural Acetylenes. Part XLIII.[1] Polyacetylenes from Cultures of the Fungus *Fistulina pallida* (Berk. and Rev.) [2]

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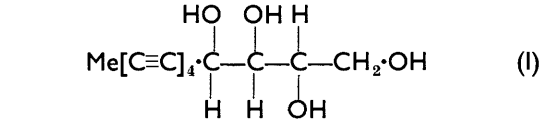
The new polyacetylenes (2*S*)-Me[CH_2]$_2$·[C≡C]$_3$·^{t}CH=CH·CH(OH)·CH_2·OH, its glucoside and 3-phenyl-lactate and HO·CH_2·^{t}CH=CH·[C≡C]$_2$·[CH_2]$_2$·CO_2H, as well as the known acids HO·CH_2·^{c}CH=CH·[C≡C]$_2$·[CH_2]$_2$·CO_2H, HO·CH_2·^{t}CH=CH·[C≡C]$_2$·[CH_2]$_2$·CO_2H, and (2*R*)-PhCH_2·CH(OH)·CO_2H have been detected in extracts from the culture fluids of *F. pallida*. The natural C_{13} diol and its *cis*-isomer have been synthesised from 2,3-*O*-isopropylidene-D-glyceraldehyde.

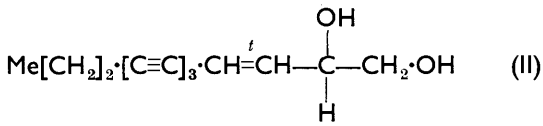
THE fungus *Fistulina hepatica* (Hudson) Fr. was found to produce polyacetylenes both in mycelial cultures [3] and in fruiting bodies in the field.[4] The C_{13} tetrayne tetraol (I) was the major polyacetylene of the culture fluid but it was not detected in the arboreal sporophores in the mixture of unidentified neutral polyacetylenes and several C_{10} acids which were found to be present. We now describe the analysis of another member of the genus, *F. pallida* (Berk. and Rev.). The fungus was grown in surface cultures and produced neutral and acidic polyacetylenes: the presence of the C_{13} triynene diol (II), its glucoside (IV) and phenyl-lactate (III), the C_{10} diynene acids (V; R = H) and (VI; R = H), and the C_9 diynene acid (VII; R = H) was established. Another diynene acid, probably the *cis*-acid (VIII; R = H), was not characterised. (2*R*)-3-Phenyl-lactic acid (IX; R = H) was the major non-polyacetylenic acid present in the extract.

The main polyacetylene, the crystalline triynene diol (II) was isolated in quantities of 1·5 mg l^{-1} of culture fluid. It gave the acetonide (X), and on periodate cleavage formaldehyde and the triynene aldehyde (XI) which, in turn, was reduced by sodium borohydride to the triynene alcohol (XII). These transformations and the associated spectral changes permitted unambiguous allocations of structures. Those of the natural product (II) and its acetonide (X) were confirmed by synthesis which was carried out to establish the stereochemistry at C(2) (see below).

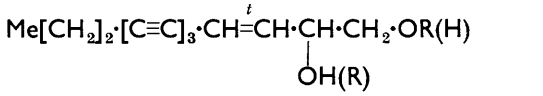
Also present in the neutral fraction were small amounts of less and more polar polyacetylenes (mainly triynenes) which could not be isolated without deterioration of the chromophore. A complex, more polar triynene fraction, with spectral features similar to those of the diol (II), was separated but attempts at simple modification of the functionality resulted in decomposition. On chromatography or in the crystalline matrix the diol (II) itself undergoes gradual decomposition to more polar materials. A variety of alcohol-protecting methods were investigated to circumvent these isolation and handling difficulties. The most successful involved conversion of the crude hydroxylic neutrals into their *O*-dimethyl-t-butylsilyl derivatives (with chlorodimethyl-t-butylsilane–dichloromethane). The use of this protecting group,[5] which is considerably more inert to hydrolysis



(I)

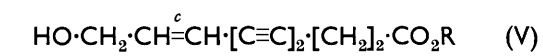


(II)



(III) R = $PhCH_2$·CH(OH)·CO

(IV) R = $C_6H_{11}O_5$



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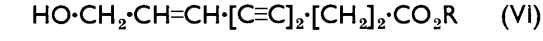

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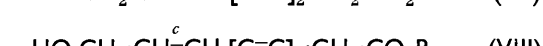

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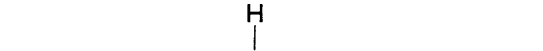
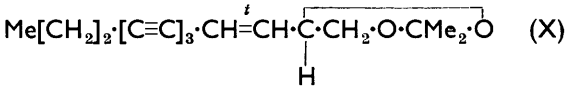
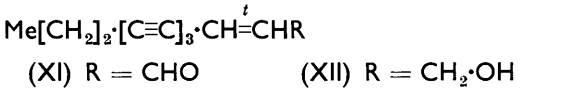


(VIII)

(IX)



(X)



(XI) R = CHO (XII) R = CH_2·OH

than the trimethylsilyl counterpart, permitted partial resolution of the minor components. From the non-polar fraction the bis-*O*-silyl derivative of the diol (II)

[1] Part XLII, M. T. W. Hearn, Sir Ewart R. H. Jones, M. G. Pellatt, V. Thaller, and J. L. Turner, *J.C.S. Perkin I*, 1973, 2785.

[2] A more detailed account of part of the work described in this paper is in the D.Phil. Thesis of G. C. Barley, Oxford, 1971.

[3] Sir Ewart R. H. Jones, G. Lowe, and P. V. R. Shannon, *J. Chem. Soc.* (*C*), 1966, 139.

[4] I. W. Farrell, J. W. Keeping, M. G. Pellatt, and V. Thaller, *J.C.S. Perkin I*, 1973, 2642.

[5] E. J. Corey and A. Venkateswarlu, *J. Amer. Chem. Soc.*, 1972, **94**, 6190.

was easily isolated and converted into the diol. The yield of the diol (II) obtained by this method was 2·5 times that obtained in the direct isolation procedure.

From more polar *O*-silyl derivative fractions small amounts of two further triynenes were obtained. Although these materials could not be isolated in a pure state, they appear to be the *O*-dimethyl-t-butylsilyl derivatives of a 3-phenyl-lactate (III) and a glucoside (IV) of the diol (II). The presence of phenyl-lactic acid and glucose was confirmed by comparing the products obtained on mild hydrolysis with authentic specimens. The site of the linkage in either the ester or the glucoside could not be determined with the available material. An enetriynene-containing fraction was also obtained but again, scarcity of material prevented identification.

Only diynene u.v. absorption was recognisable in the esterified acid fraction. On repeated chromatography of the complex methyl ester mixture the presence of the C_{10} esters (V; R = Me) and (VI; R = Me) and the C_9 ester (VII; R = Me) was ascertained. Two more polar diynenes were also detected, one of them being possibly the C_9 ester (VIII; R = Me). The natural *trans*-esters were identical with synthetic specimens prepared for comparison by esterification of the products of Chodkiewicz coupling between 5-bromopent-*trans*-2-en-4-yn-1-ol and pent-4-ynoic acid and but-3-ynoic acid, respectively.

The C_9 *trans*-ester (VII; R = Me) has been previously isolated from *Poria selecta*.[6] The C_{10} *cis*-ester (V; R = Me) was isolated from the sporophores of *F. hepatica*.[4] Reinvestigation of the polyacetylenic esters obtained from the fruiting bodies has now confirmed that, in common with *F. pallida*, both the *cis*- and *trans*-C_{10} esters are present.

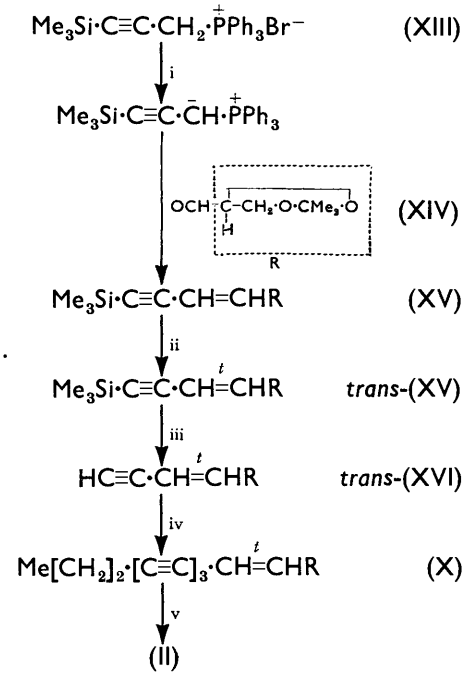
Methyl (2*R*)-3-phenyl-lactate (IX; R = Me) was the main component of the ester mixture. The *S*-acid was previously isolated [7] from culture broths of *Exobasidium symploci* and found to act as plant growth regulator (the *R*-enantiomer was inactive).

The route employed in the synthesis of the diol (II) is shown in the Scheme. 2,3-*O*-Isopropylidene-D-glyceraldehyde (XIV) and the ylide derived from the trimethylsilylphosphonium salt (XIII) gave the trimethylsilyl enyne acetonide (XV) in a *cis–trans* ratio of 5 : 1 at −78° and 1·25 : 1 at −40° [*cf.* the more favoured *trans*-double bond formation with other aldehydes reported by Corey [8] and the selective *cis*-double bond formation in the skipped enyne synthesis from the corresponding butynyl salt (XVII) [9]]. The two isomers were separated by chromatography and the *trans*-enyne (XV) was converted into the *trans*-triynene acetonide (X) and the diol (II). The synthetic specimens and the natural diol and its acetonide were identical in all respects including the signs of the o.r.d. curves (589—436 nm): the natural diol (II) must thus have the (2*S*)-configuration [*cf.* the opposite configuration at C(2) in the tetraol (I)].

[6] R. E. Bew, R. C. Cambie, Sir Ewart R. H. Jones, and G. Lowe, *J. Chem. Soc.* (*C*), 1966, 135.

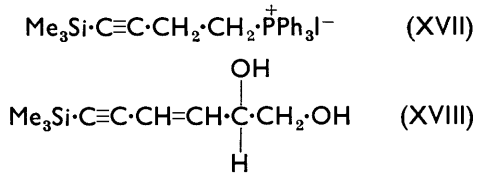
[7] S. Tamura and C. Chang, *Agric. and Biol. Chem.* (*Japan*), 1965, **29**, 1061 (*Chem. Abs.*, 1966, **64**, 5352h).

The *trans*- and *cis*-dioxolans (XV) showed opposite trends in their o.r.d. curves in the visible spectrum, and the same was observed when the *cis*-dioxolans (XVI) and (X) were prepared. Inversion of rotation like that observed when the natural *trans*-diol (II) was converted into its acetonide (X) and *vice versa* did not occur on



SCHEME Reagents: i, Bu^nLi–$[CH_2]_4O$; ii, SiO_2 chromatography; iii, $AgNO_3$–EtOH, KCN; iv, CuCl, $EtNH_2$, NH_2·OH,HCl, $Me[CH_2]_2·[C≡C]_2·Br$; v, HCl–EtOH

hydrolysis of the *cis*-dioxolan (X) to the parent *cis*-diol (II). It did occur, however, with both the *trans*- and *cis*-dioxolan (XV) on conversion into the parent diols (XVIII). The influence of double-bond stereochemistry in polyacetylenes on the optical rotatory power of allylic asymmetric centres is being further studied.



In the n.m.r. spectrum the three dioxolan ring protons were differently shielded and gave rise to triplet- and double-doublet-like signals in the τ 5—6·8 region. Spin–spin decoupling experiments on the *trans*-dioxolan (XV) confirmed the expectation that the apparent coupling constants quoted are not of the first order but conceal much more complex spectra of the ABC type which have not been analysed.

[8] E. J. Corey and R. A. Ruden, *Tetrahedron Letters*, 1973, 1495.

[9] A. G. Fallis, M. T. W. Hearn, Sir Ewart R. H. Jones, V. Thaller, and J. L. Turner, *J.C.S. Perkin I*, 1973, 743.

EXPERIMENTAL

Instruments used: u.v., Unicam SP 800; i.r., Unicam SP 1000 and Perkin-Elmer 257; n.m.r., Perkin-Elmer R10 and R14; mass spectra (direct insertion) Varian-MAT CH7 and A.E.I. MS9; specific rotations, Perkin-Elmer 141; m.p.s (corr.), Kofler hot-stage apparatus.

Solution chromatography: SiO_2 H.B.L. M60 in columns and Merck $HF_{254+366}$ and $PF_{254+366}$ in 0·3 mm (t.l.c.) and 1 mm (p.l.c.) layers, respectively.

Petrol refers to light petroleum of b.p. 30—40°.

Growth and Extraction of Fistulina pallida (*Berk. and Rev.*) *Cultures and General Work-up of Extracts.*—The fungus was grown on 3% malt extract in surface cultures supported on glass wool. When maximum polyacetylene concentrations (estimated by u.v.) were reached (40—45 days), the medium was decanted and replaced by a 4% solution of glucose containing sodium acetate (0·2M). In this, maximum polyacetylene production occurred within 12—15 days after reflooding; the reflood procedure was repeated until a decline in polyacetylene production was observed. The culture fluids and the glucose–acetate reflood fluids were each continuously extracted with Et_2O (48 h); the extracts were concentrated to 200—300 ml and separated into neutral and acidic fractions ($NaHCO_3$); and the latter was esterified with 4% H_2SO_4 in MeOH.

Neutral Fraction.—This exhibited strong triynene u.v. absorption. T.l.c. of the culture fluid extract indicated a mixture of materials with one major component (R_F 0·4; Et_2O, two elutions), whilst the reflood extract contained essentially one polyacetylene of similar polarity. In a typical isolation procedure the concentrated neutral material from the culture fluid of 30 flasks (660 mg) was separated on a SiO_2 column (250 g) by stepwise elution (petrol–Et_2O, 1 : 1, to Et_2O–MeOH, 1 : 1; 4 l) and 100 ml fractions were collected. Fractions showing the same composition (t.l.c.) were combined and subjected to p.l.c. (Et_2O, multiple elutions, or EtOAc). Fractions 14—20 yielded thus on crystallisation (Et_2O–petrol) the major neutral component (2S)-*tridec*-trans-3-*ene*-5,7,9-*triyne*-1,2-*diol* (II) (42 mg), m.p. 98—98·5° (reddens near 70°) (Found: C, 77·2; H, 7·0. $C_{13}H_{14}O_2$ requires C, 77·3; H, 7·0%), $[\alpha]^{20}$ −9·85 (589 nm), −10·7 (578), −12·1 (546), and −20·3° (436) (*c* 0·5 in EtOH), $\lambda_{max.}$ (EtOH) 331 (ε 12,000), 309 (17,300), 290 (12,900), 273 (7300), 259 (4200), 244 (97,000), 233 (59,000), 225infl., and 213 (280,000) nm, $\nu_{max.}$ ($CHCl_3$) 3550 and 3400br (free and bonded OH), 2250 and 2130 (C≡C), and 965 (*trans*-CH=CH) cm^{-1}, τ ($CDCl_3$) 9·00 (3H, t, *J* 7 Hz, $CH_3{\cdot}CH_2$), 8·40 (2H, sextet, *J* 7 Hz, $CH_3{\cdot}CH_2{\cdot}CH_2$), 7·72 (2H, t, *J* 7 Hz, $CH_2{\cdot}CH_2{\cdot}C{\equiv}C$), 6·35 (2H, m, $CH_2{\cdot}CH_2{\cdot}OH$), 5·64 [1H, m, $C{=}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}O$], 4·08 (1H, d, *J* 16 Hz, $C{\equiv}C{\cdot}CH{=}CH$), and 3·63 (1H, dd, *J* 16 and 6 Hz, $CH{-}CH{\cdot}CHO$), *m/e* 202 (M^+, 4%), 172 (28), 171 (100), 152 (18), 140 (20), 128 (90), 115 (52), 101 (10), 87 (15), 75 (13), and 63 (10).

Subsequent more polar fractions contained material exhibiting mixed chromophores (most likely triynene, enetriynene, and tetrayne). The production of these materials which represented *ca.* 10% of the polyacetylene content was variable between growths and the components could not be separated without decomposition.

Silylation of the Diol (II) *and the Neutral Fraction.*—(*a*) The diol (II) (20 mg), chlorodimethyl-t-butylsilane (45 mg), and imidazole (34 mg) were stirred in CH_2Cl_2 (50 ml) at 20° for 12 h. Filtration, washing of the filtrate (0·1N-HCl; 50 ml), concentration, and p.l.c. (cyclohexane) of the residue gave the liquid *bis*-O-*silyl diol* (II) (32 mg), R_F 0·90 [Found: *m/e*, 373·202. $C_{21}H_{33}Si_2O_2$ ($C_{25}H_{42}Si_2O_2 - C_4H_9$) requires *m/e*, 373·2019], $\lambda_{max.}$ (EtOH) 330·5 (ε 11,500), 309 (16,300), 290 (12,800), 273 (8300), 258 (6000), 245 (105,000), and 232·5 (64,000) nm, $\nu_{max.}$ (CCl_4) 2225 and 2190 (C≡C), 1280 (O–Si), and 955 (*trans*-CH=CH) cm^{-1}, τ (CCl_4) 9·95 (12H, s, $SiMe_2$), 9·15 (18H, s, Bu^t), 9·01 (3H, t, *J* 7 Hz, $CH_3{\cdot}CH_2$), 8·44 (2H, sextet, *J* 7 Hz, $CH_3{\cdot}CH_2{\cdot}CH_2$), 7·73 (2H, t, *J* 7 Hz, $CH_2{\cdot}CH_2{\cdot}C{\equiv}C$), 6·57 (2H, m, $CH_2{\cdot}OSi$), 5·84 (1H, m, $CH{\cdot}OSi$), 4·30 (1H, d, *J* 16 Hz, $C{\equiv}C{\cdot}CH{=}CH$), and 3·68 (1H, dd, *J* 16 and 4 Hz, $C{\equiv}C{\cdot}CH{-}CH{\cdot}CHO$), *m/e* 430 ($M^+$, 2%), 415 (1), 387 (6), 373 (13), 331 (10), 323 (31), 299 (4), 289 (24), 285 (22), 234 (13), 201 (6), 147 (95), 133 (28), 117 (100), and 115 (15).

(*b*) The concentrated neutral fraction from 30 flasks (710 mg; estimated by u.v. to contain *ca.* 320 mg of polyacetylenes) in CH_2Cl_2 (50 ml) was added to chlorodimethyl-t-butylsilane [600 mg, *ca.* 2·5 mmol. equiv. based on the diol (II)] and imidazole (680 mg) in CH_2Cl_2 (25 ml) cooled to 0°. After 24 h, the mixture was washed with 0·1N-HCl (50 ml) and H_2O, and concentrated, and the residue (900 mg) was separated by p.l.c. (cyclohexane) into seven bands. Each band was repeatedly rechromatographed on SiO_2 or SiO_2–$AgNO_3$ plates. The major band (R_F 0·90) yielded the bis-*O*-silyl diol (II) (376 mg). A sample of this (64 mg) and $(Bu^n)_4NF^-$ (200 mg) were stirred in anh. C_4H_8O (20 ml) for 4 h at 25°. Et_2O extraction and crystallisation (Et_2O–petrol) gave the diol (II) (17 mg, 57%), m.p. and mixed m.p. 97—97·5°, equivalent to 100 mg of diol (II) from 30 flasks.

Bands 2 (R_F 0·8) and 3 (R_F 0·7) both exhibited strong triynene absorption but on rechromatography appeared to be complex mixtures of polyacetylenes. From band 2 a crude ester (17 mg), $\nu_{max.}$ (CCl_4) 2220 and 2190 (C≡C), 1740 (ester CO), 1290 (O–Si), and 960 (*trans*-CH=CH) cm^{-1}, was obtained. The ester (15 mg) was kept at 40° for 4 h with N-HCl (1 ml) and yielded on partition into neutral and acidic products the diol (II) (3 mg) and 3-phenyl-lactic acid (2 mg), m.p. 122—124° (lit.,[10] 122° for *R*-acid), $\nu_{max.}$ (Nujol) 3440 and 2500—3100 (OH and CO_2H) and 1730 (acid CO) cm^{-1}, *m/e* 166 (M^+ 40%).

A diffuse triynene-containing band (R_F 0·05—0·15) was isolated and yielded a yellow oil (31 mg). This was kept in 4N-HCl (1 ml) at 40° for 2 h; the mixture was extracted with Et_2O, and the extract yielded the diol (II) (7 mg). On concentration of the aqueous phase a residue was obtained which on paper chromatography (Whatman no. 1; Me_2CO–H_2O–HCO_2H, 81 : 6 : 13) behaved identically with glucose. Attempts to obtain a fully silylated pure glycoside were unsuccessful.

Acidic Fraction.—The concentrated acidic fraction was esterified with 4% H_2SO_4–MeOH. The combined methyl esters from several growths (90 flasks; 1·64 g) (enediyne absorption) were separated on a SiO_2 column (150 g) by stepwise elution (petrol–Et_2O, 99 : 1, to Et_2O–MeOH, 3 : 1, 5 l). 100 ml Fractions were collected. Those exhibiting enediyne absorption were combined and separated by p.l.c. (petrol–Et_2O, 1 : 1) into two major fractions, A (R_F 0·65) and B (R_F 0·55). P.l.c. of fraction A on 10% $AgNO_3$–SiO_2 (petrol–Et_2O, 3 : 1; 4 elutions) yielded methyl 9-hydroxy-non-*trans*-7-ene-3,5-diynoate (VII) [6] (7 mg), m.p. and mixed m.p. 53—55° (Et_2O–petrol). A second, slightly more polar compound (*ca.* 1 mg), $\lambda_{max.}$ (Et_2O) 281 (rel. *E* 12·0), 266 (15·0), 252 (9·0), 234 (3·3), and 227 (1·0) nm, $\nu_{max.}$ (CCl_4)

[10] D. Biquard, *Ann. Chim.* (*France*), 1933, **20**, 97.

3600 (OH), 2220 (C≡C), and 1745 (ester CO) cm^{-1}, $\nu_{max.}$ (CS_2) 730 (*cis*-CH=CH) cm^{-1}, could be the *cis*-ester (VIII).

Analogous work-up of fraction B gave methyl 10-hydroxydec-*trans*-8-ene-4,6-diynoate (VI) (27 mg), identical with a synthetic specimen (see below), and methyl 10-hydroxydec-*cis*-8-ene-4,6-diynoate (V) [4] (51 mg), m.p. *ca.* 0°, $\lambda_{max.}$ (EtOH) 283 (ε 12,000), 267 (15,000), 253 (10,500), 235 (4800), and 228 (2000) nm; the remaining spectra were identical with those described.

Two more polyacetylene-containing bands at R_F 0·40 (enediynene) and R_F 0·2 (enediyne) were detected: the amount of polyacetylenes present was too small for further investigation.

Fractions immediately preceding the polyacetylenes exhibited benzenoid absorption (u.v.). They were combined and yielded on concentration, p.l.c. (petrol–Et_2O, 3 : 1; 4 elutions), and crystallisation (Et_2O–petrol) needles of methyl (2*R*)-3-phenyl-lactate (IX; R = Me) (187 mg), m.p. 47·5—48° (lit.,[10] 48·5°) (Found: C, 66·3; H, 6·7. Calc. for $C_{10}H_{12}O_3$: C, 66·6; H, 6·7%), $[\alpha]^{20}$ −8·4 (589 nm), −8·8 (578), −10 (546), −21·3 (436), and −43° (365) (*c* 0·01 in EtOH) {lit.,[11] $[\alpha]^{16·3}$ −5·25 (579 nm), −6·31 (546), and −15·05° (436) (*c* 21·01 in EtOH)}, $\nu_{max.}$ (CCl_4) 3250, 1750, and 1735 cm^{-1}, τ (CCl_4) 7·06 (2H, d, *J* 6 Hz, CH_2·CHO), 6·31 (3H, s, CO_2·CH_3), 5·66 (1H, t, *J* 6 Hz, CH_2·*CH*·OH), and 2·85 (5H, s, C_6H_5), *m/e* 180 (M^+, 3%), 162 (35), 131 (11), 121 (19), 103 (20), and 91 (100).

(4S)-2,2-*Dimethyl*-4-(*undec*-trans-1-*ene*-3,5,7-*triynyl*)-1,3-*dioxolan* (X).—The diol (II) (46·5 mg), anh. $CuSO_4$ (200 mg), and *p*-MeC_6H_4·SO_3H (2 mg) were shaken in Me_2CO (20 ml) for 12 h under N_2 in the dark. K_2CO_3 addition, filtration, and p.l.c. (Et_2O–petrol, 1 : 1; 2 elutions) of the concentrated filtrate yielded the *acetonide* (X) (32 mg, 57%), R_F 0·7 (Found: M^+, 242·13064. $C_{16}H_{18}O_2$ requires *M*, 242·1307), $[\alpha]^{20}$ +55·5 (589 nm), +59·5 (578), +70 (546), and +124·5° (436) (*c* 0·25 in EtOH), $\lambda_{max.}$ (EtOH) 332 (ε 13,500), 311 (17,800), 292 (13,200), 275 (6500), 260 (3000), 246 (48,700), and 234 (31,300) nm, $\nu_{max.}$ (CCl_4) 2230 and 2200 (C≡C) and 952 (*trans*-CH=CH) cm^{-1}, τ (CCl_4) 8·98 (3H, t, *J* 7 Hz, CH_3·CH_2), 8·70 and 8·65 (each 3H, s, CH_3·C·CH_3), 8·42 (2H, sextet, *J* 7 Hz, CH_3·CH_2·CH_2), 7·70 (2H, t, *J* 7 Hz, CH_2·CH_2·C≡C), 6·49 [1H, t, *J* 7 Hz, OCH·C(H)*H*·O], 5·97 [1H, dd, *J* 7 and 7 Hz, O·CH·C(*H*)H·O], 5·54 [1H, m, =CH·C*H*(O)·CH_2·O], 4·26 (1H, d, *J* 17 Hz, C≡C·C*H*=CH), and 3·75 (1H, dd, *J* 6 and 17 Hz. CH=C*H*·CHO), *m/e* 242 (M^+, 5%), 122 (100), 107 (36), 93 (44), 79 (26), and 67 (31).

Periodate Cleavage of the Diol (II).—The diol (II) (24·7 mg) and $NaIO_4$ (100 mg) were shaken in H_2O (20 ml), Et_2O (8 ml), and hexane (2 ml) under N_2 in the dark for 5 h. The H_2O layer was distilled into dimedone solution. Crystals separated, m.p. and mixed m.p. with authentic CH_2O–dimedone, 189—192°. The concentrated solvent layer yielded on crystallisation (petrol at −20°) pale yellow needles of *dodec*-trans-2-*ene*-4,6,8-*triynal* (XI) (16 mg, 76%), m.p. 65—66° (Found: M^+, 170·0732. $C_{12}H_{10}O$ requires *M*, 170·0732), $\lambda_{max.}$ (Et_2O) 349 (ε 15,700), 326 (19,500), 306·5 (12,700), 289 (5700), 265·5 (48,500), and 248 (30,500) nm, $\nu_{max.}$ (CCl_4) 2720 (CHO), 2225, 2200, and 2120 (C≡C), 1690 (CHO), and 953 (*trans*-CH=CH) cm^{-1}, τ (CCl_4) 8·96 (3H, t, *J* 6 Hz, CH_3·CH_2), 8·37 (2H, m, CH_3·CH_2·CH_2), 7·65 (2H, t, *J* 6 Hz, CH_2·CH_2·C≡C), 3·45 (2H, m, C≡C·C*H*=C*H*·CHO), and 0·41 (1H, *J* 3 Hz, CH=CH·C*H*O), *m/e* 170 (M^+, 100%), 141 (80), 115 (95), 113 (30), 100 (32), and 87 (65).

The aldehyde (XI) (22 mg) and $NaBH_4$ (50 mg) were stirred in MeOH (5 ml) at 0° under N_2 for 2 h. The product was then isolated with Et_2O and crystallised (Et_2O–petrol) to yield needles of *dodec*-trans-2-*ene*-4,6,8-*triyn*-1-*ol* (19·1 mg, 85%), m.p. 77—78° (Found: M^+, 172·0884. $C_{12}H_{12}O$ requires *M*, 172·0888), $\lambda_{max.}$ (Et_2O) 329 (ε 10,700), 308 (16,600), 289·5 (12,500), 273 (6500), 258 (3000), 244 (100,000), and 232 (62,000) nm, $\nu_{max.}$ ($CHCl_3$) 3600 and 3200 (OH), 2230 (C≡C), and 950 (*trans*-CH=CH) cm^{-1}, τ (CCl_4) 8·97 (3H, t, *J* 7 Hz, CH_3·CH_2), 8·38 (2H, m, CH_3·CH_2·CH_2), 7·67 (2H, t, *J* 7 Hz, CH_2·CH_2·C≡C), 5·78 (2H, d, *J* 6 Hz, CH_2·OH), 4·16 (1H, d, *J* 16 Hz, C≡C·C*H*=CH), and 3·61 (1H, dt, *J* 6 and 16 Hz, CH=C*H*·CH_2·OH), *m/e* 172 (M^+, 85%), 128 (100), 127 (41), and 115 (82).

Triphenyl-(3-*trimethylsilylprop*-2-*ynyl*)*phosphonium Bromide* (XIII).—Prop-2-yn-1-ol (28 g, 0·5 mol) in $[CH_2]_4O$ (150 ml) was added dropwise to EtMgBr {from Mg (24·4 g) and EtBr (110 g) in $[CH_2]_4O$ (150 ml)} stirred at 0° (ice–water cooling). Stirring was continued for 1·5 h and Me_3SiCl (110 g) was then added dropwise over 1 h. The mixture was kept at 50° for 1 h and at 20° for 12 h; after addition of sat. NH_4Cl in H_2O (800 ml) it was extracted with Et_2O (3 × 400 ml). The extract was washed (brine) and concentrated, and the residue was stirred with ice (30 g)–EtOH (100 ml)–HCl (conc., 10 drops) for 1 h. Et_2O extraction and fractional distillation yielded 3-trimethylsilylprop-2-yn-1-ol (27·7 g, 50%), b.p. 77·5—78° at 12 mmHg (lit.,[12] 76° at 11 mmHg), $\nu_{max.}$ (CCl_4) 3600 and 3450 (free and bonded OH) and 2185 (C≡C) cm^{-1}, τ (CCl_4) 9·85 (9H, s, Me_3Si), 7·95 (1H, s, OH), and 5·85 (2H, s, C≡C·CH_2·OH), *m/e* 128 (M^+, 2%), 113 (82), 85 (100), 75 (30), 73 (22), and 61 (36).

This (5·16 g, 40 mmol) in Me_2N·CHO (20 ml) was added to Ph_3PBr_2 [13] [from Br_2 (3·35 ml, 60 mmol) and Ph_3P (24 g, 91 mmol)] stirred in Me_2N·CHO (100 ml) under N_2 at 0°. Stirring was continued first at 0° (3 h) and then at 20° (12 h). The mixture was extracted with petrol (3 × 100 ml); the extract was washed with $NaHCO_3$–H_2O, dried, filtered, and concentrated, and the liquid residue was chromatographed on SiO_2 (120 g) from petrol. Concentration of the eluate and fractional distillation gave 3-bromo-1-trimethylsilylprop-1-yne (5·6 g, 71%), b.p. 44—45° at 2 mmHg, R_F 0·73 (petrol–Et_2O) (Found: C, 38·25; H, 5·95; Br, 42·45. $C_6H_{11}BrSi$ requires C, 37·7; H, 5·75; Br, 41·9%), $\nu_{max.}$ (CCl_4) 2180 (C≡C) cm^{-1}, τ (CCl_4) 9·85 (9H, s, MeSi) and 6·17 (2H, s, CH_2Br).

The bromide (2·0 g, 10·5 mmol) and Ph_3P (3·56 g, 13·6 mmol) were stirred in C_6H_6 (20 ml) in the dark at 20° for 18 h. The precipitate was filtered off, washed with petrol, and dried (30—40° at 0·2 mmHg for 8 h) to yield the *phosphonium bromide* (XIII) (3·2 g, 67%), m.p. 154—156° (Found: C, 63·9; H, 5·9. $C_{24}H_{26}BrPSi$ requires C, 63·6; H, 5·7%). An attempt to recrystallise the Wittig salt (MeOH–EtOAc–hexane) led to decomposition, so the crude, dried salt was used directly in the Wittig reaction.

2,3-O-*Isopropylidene*-D-*glyceraldehyde* (XIV).—$NaIO_4$ (0·58 g, 2·6 mmol) in H_2O (20 ml), treated with a little $NaHCO_3$ (cloudiness) was shaken with a suspension of 1,2,5,6-di-*O*-isopropylidene-D-mannitol [14] (312 mg, 1·19

[11] D. Biquard, *Ann. Chim.* (*France*), 1933, **20**, 153. For allocation of configuration *cf.* 'Beilsteins Handbuch der Kohlenstoffverbindungen,' 4th edn., 3rd supplement, vol. 10, Springer-Verlag, Berlin–Heidelberg–New York, 1971, p. 556.

[12] M. F. Shostakovskii, N. V. Komarov, and O. G. Yarosh, *Bull. Acad. Sci. U.S.S.R.*, 1966, 79.

[13] G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, 1964, **86**, 964.

[14] E. Baer, *J. Amer. Chem. Soc.*, 1945, **67**, 338.

mmol) in Et_2O (20 ml) for 15 min. The layers were separated and the H_2O layer was saturated with NaCl and extracted with Et_2O (3 × 50 ml). The combined extracts were dried (K_2CO_3) and concentrated. The crude aldehyde (XIV), R_F 0·25 (Et_2O), $[\alpha]^{20}$ +45·5 (588 nm), +46 (578), +55 (546), and +116° (436) (*c* 0·777 in benzene) {lit.,[15] $[\alpha]_D^{21}$ +64·9° (*c* 5·73 in benzene) for distilled aldehyde}, $\nu_{max.}$ 1740 (CO) and 1385 and 1365 (CMe_2) cm^{-1}, τ (CCl_4) 8·6 and 8·5 (each s, CMe_2), 5·9 and 5·7 (each m, $OCH{\cdot}CH_2{\cdot}O$), and 0·3 (s, CHO), was used in the Wittig reaction.

trans- *and* cis-(4S)-2,2-*Dimethyl*-4-(4-*trimethylsilylbut*-1-*en*-3-*ynyl*)-1,3-*dioxolan* [trans- *and* cis-(XV)].—The Wittig salt (XIII) (1·836 g, 4·05 mmol) was suspended in dry $[CH_2]_4O$ (20 ml) under N_2 at −78° and Bu^nLi in hexane (2·2 ml, 4·1 mmol) was added over 5 min. The mixture was kept at −40° for 0·5 h, then cooled again to −78°, and 2,3-*O*-isopropylidene-D-glyceraldehyde (XIV) (from 1·19 mmol of di-isopropylidene-D-mannitol) in dry $[CH_2]_4O$ (2 ml) was added slowly to it. After 1 h at −78° and 1 h at 0°, Et_2O (50 ml) was added to the mixture, the solids were removed by filtration, and the filtrate was concentrated. The residue was separated by p.l.c. (5% Et_2O–petrol; continuous elution) into two bands with R_F 0·7 and 0·5, respectively. The less polar band yielded the cis-*dioxolan* [*cis*-(XV)] (214 mg, 0·95 mmol, 40% from di-isopropylidenemannitol), b.p. 58—60° (bath) at 1 mmHg (Found: C, 64·5; H, 9·0. $C_{12}H_{20}O_2Si$ requires C, 64·3; H, 8·9%), $[\alpha]^{20}$ −3·8 (589 nm), −4·2 (578), −5·5 (546), −23 (436), and −72° (365) (*c* 1·837 in EtOH), $\lambda_{max.}$ (Et_2O) 247 (ε 11,100), 236 (13,300), and 227 (9300) nm, $\nu_{max.}$ (CCl_4) 2150 (C≡C) cm^{-1}, $\nu_{max.}$ (CS_2) 780 (*cis*-CH=CH) cm^{-1}, τ (CCl_4) 9·97 (9H, s, Me_3Si), 8·86 (6H, s, Me_2C), 6·70 [1H, t, *J* 8 Hz, $CH{\cdot}CH(H)O$], 6·08 [1H, dd, *J* 7 and 8 Hz, $CH{\cdot}CH(H)O$], 5·29 [1H, q, *J* 8 Hz, $CH{=}CH{\cdot}CH(O){\cdot}CH_2$], 4·70 (1H, d, *J* 11 Hz, C≡C·*CH*=CH-*cis*), and 4·27 (1H, dd, *J* 11 and 8 Hz, $CH{=}CH{\cdot}CHO$), *m/e* 224 (M^+, 5%), 209 (10), 167 (10), 166 (15), 151 (37), 109 (48), 97 (15), 83 (25), 73 (100), and 72 (45).

The more polar band yielded the trans-*dioxolan* [*trans*-(XV)] (43 mg, 0·2 mmol, 9% from di-isopropylidenemannitol), b.p. 60—62° (bath) at 1 mmHg (Found: C, 64·3; H, 9·2%), $[\alpha]^{20}$ +55 (589 nm), +58 (578), +67 (546), +123 (436), and +206° (365) (*c* 0·457 in EtOH), $\lambda_{max.}$ (Et_2O) 246 (ε 19,600), 235 (23,700), and 226 (16,700) nm, $\nu_{max.}$ (CCl_4) 2160 and 2130 (C≡C) and 950 (*trans*-CH=CH) cm^{-1}, τ (CCl_4) 9·97 (9H, s, Me_3Si), 8·88 and 8·83 (each 3H, s, $CH_3{\cdot}C{\cdot}CH_3$), 6·62 [1H, t, *J* 8 Hz, $CH{\cdot}CH(H)O$], 6·13 [1H, dd, *J* 7 and 8 Hz, $CH{\cdot}CH(H)O$–], 5·70 [1H, qm, *J* 7 Hz, $=CH{\cdot}CH(O){\cdot}CH_2$], 4·48 (1H, d, *J* 17 Hz, C≡C·*CH*=CH), and 4·09 (1H, dd, *J* 17 and 6 Hz, C≡C·CH=*CH*·CHO), τ (C_6H_6) 6·99 (complex t, *J* 8 Hz), 6·61 (dd, *J* 7 and 9 Hz), 6·12 (qm, *J* 7 Hz), 4·51 (d, *J* 17 Hz), and 4·17 (dd, *J* 7 and 17 Hz) [on irradiation around τ 6·12 the triplet at τ 6·99 changed into a very different multiplet, and on irradiation at τ 6·99 the quadruple multiplet collapsed into a double multiplet with *J ca.* 7 Hz], *m/e* 224 (M^+, 5%), 209 (10), 151 (12), 109 (30), 73 (75), and 43 (100).

When the aldehyde (XIV) was added to the phosphorane at −40° and the mixture was kept for 1 h at 0° the combined yield of the *cis*- and *trans*-dioxolans (XV) was 42% and the *cis*–*trans* ratio was 1·25 : 1.

(4S)-4-(*But*-trans-1-*en*-3-*ynyl*)-2,2-*dimethyl*-1,3-*dioxolan* [*trans*-(XVI)].—To the silyldioxolan [*trans*-(XV)] (177 mg, 0·79 mmol) in EtOH (15 ml) stirred at 0° under N_2 was added dropwise $AgNO_3$ (552 mg, 3·25 mmol) in EtOH–H_2O (20 ml; 1 : 1) over 30 min. After 1 h at 0°, KCN (1·5 g) in H_2O (5 ml) was added and the product was isolated with Et_2O. Purification by p.l.c. (Et_2O–petrol, 1 : 19; 2 elutions) gave the trans-*ethynyl acetonide* [*trans*-(XVI)] (48 mg, 39%), $[\alpha]^{21}$ +11 (589 nm), +11 (578), +13 (546), +24 (436), and +38° (365) (*c* 0·755 in EtOH), $\lambda_{max.}$ (Et_2O) 232sh (ε 6100) and 224 (7500) nm, $\nu_{max.}$ (CCl_4) 3310 (C≡CH) and 955 (*trans*-CH=CH) cm^{-1}, τ (CCl_4) 8·67 and 8·64 (each 3H, s, $CH_3{\cdot}C{\cdot}CH_3$), 7·23 (1H, d, *J* 1·5 Hz, C≡CH), 6·47 [1H, t, *J* 8 Hz, $OCH{\cdot}CH(H){\cdot}O$], 5·97 [1H, dd, *J* 7 and 8 Hz, $O{\cdot}CH{\cdot}CH(H){\cdot}O$], 5·55 [1H, qm, *J* 7 Hz, $=CH{\cdot}CH(O){\cdot}CH_2$], 4·35 (1H, dd, *J* 1·5 and 16 Hz, HC≡C·*CH*=CH), and 3·89 (1H, dd, *J* 6 and 16 Hz, C≡C·CH=*CH*·CH), *m/e* 152 (M^+, 2%), 137 (45), 122 (45), 107 (40), 95 (10), 94 (16), 93 (15), 79 (50), 77 (30), 72 (60), 66 (60), 65 (60), 63 (55), 59 (43), 52 (40), 51 (60), and 43 (100).

(4S)-2,2-*Dimethyl*-4-(*undec*-trans-1-*ene*-3,5,7-*triynyl*)-1,3-*dioxolan* (X).—The *trans*-dioxolan [*trans*-(XVI)] (86 mg, 0·16 mmol) in MeOH (0·6 ml) was added over 5 min to a stirred solution of CuCl (6 mg), NH_2OH,HCl (85 mg), and $EtNH_2$ (40% in H_2O; 2 ml) in MeOH (2 ml)–$Me_2N{\cdot}CHO$ (0·5 ml) under N_2 at 10°. After 5 min, 1-bromohepta-1,3-diyne (144 mg, 0·84 mmol) (for preparation see below) in MeOH (1 ml) was added dropwise over 10 min. The mixture was stirred at 10° for 1 h, then KCN (100 mg), H_2O (6 ml), and ice (3 g) were added. Isolation by Et_2O extraction (4 × 10 ml) and p.l.c. (Et_2O–petrol, 1 : 19) yielded the *trans*-triynene acetonide (X) (77 mg, 56%), $[\alpha]^{20}$ +41 (589 nm), +44·5 (578), +53 (546), and +108° (436) (*c* 0·239 in EtOH); the u.v., i.r., n.m.r., and mass spectra were identical with those quoted above.

(2S)-*Tridec*-trans-3-*ene*-5,7,9-*triyne*-1,2-*diol* (II).—The synthetic *trans*-dioxolan (X) (50 mg) was stirred for 3 h in EtOH (10 ml)–HCl (2N; 2·5 ml) under N_2 at 20°. H_2O (50 ml) addition, Et_2O extraction, chromatography (SiO_2 column, 10 g; Et_2O) and crystallisation (Et_2O–petrol) gave the diol (II), m.p. and mixed m.p. 96—97°, $[\alpha]^{20}$ −6 (589 nm), −7 (578), −8·5 (546), and −12·5° (436) (*c* 0·571 in EtOH); the spectra were identical with those of the natural product.

(2S)-6-*Trimethylsilylhex*-trans-3-*en*-5-*yne*-1,2-*diol* [*trans*-(XVIII)].—*p*-$MeC_6H_4{\cdot}SO_3H$ (15 mg) and the dioxolan [*trans*-(XV)] (48 mg, 0·22 mmol) were stirred in MeOH (3 ml) under N_2 in the dark at 20° for 2 h. Concentration and p.l.c. (Et_2O) gave the *trans*-trimethylsilyl diol [*trans*-(XVIII)] (32 mg, 81%), R_F 0·33, $[\alpha]^{20}$ −20 (589 nm), −21·5 (578), −24·5 (546), −46 (436), and −82° (365) (*c* 0·578 in EtOH), $\lambda_{max.}$ (Et_2O) 246 (ε 12,300), 236 (15,300), and 226 (11,200) nm, $\nu_{max.}$ (CCl_4) 3600 (OH), 2130 (C≡C), and 955 (*trans*-CH=CH) cm^{-1}, τ ($CDCl_3$) 9·80 (9H, s, $SiMe_3$), 7·4 (2H, s, $HO{\cdot}CH{\cdot}CH_2{\cdot}OH$; disappears on addn. of D_2O), 6·15—6·65 (2H, m, $CH{\cdot}CH_2{\cdot}OH$), 5·55—5·80 (1H, m, $O{\cdot}CH{\cdot}CH_2{\cdot}O$), 4·18 (1H, d, *J* 16 Hz, C≡C·*CH*=CH), and 3·84 (1H, dd, *J* 5 and 16 Hz, CH=*CH*·CH), *m/e* 169 (M^+ − 15, 50%), 153 (M^+ − CH_2OH, 100), 125 (55), 75 (69), and 73 (67).

(4S)-4-(*But*-cis-1-*en*-3-*ynyl*)-2,2-*dimethyl*-1,3-*dioxolan* [*cis*-(XVI)].—The *cis*-trimethylsilyl dioxolan [*cis*-(XV)] (200 mg, 0·9 mmol) was desilylated analogously to the *trans*-isomer and gave the cis-*ethynyl acetonide* [*cis*-(XVI)] (87 mg, 64%), $[\alpha]^{20}$ −6·5 (589 nm), −7·0 (578), −9 (546), −29 (436), and −82° (365) (*c* 0·332 in EtOH), $\lambda_{max.}$ 233 sh (ε 7600) and 225 (8600) nm, $\nu_{max.}$ (CCl_4) 3310 (C≡CH), 3040 (CH=CH), and 2100 (C≡C) cm^{-1}, $\nu_{max.}$ (CS_2) 3310 (C≡CH) and 750 (*cis*-CH=CH) cm^{-1}, τ (CCl_4) 8·68 (6H, s, $CH_3{\cdot}C{\cdot}CH_3$), 6·95 (1H, d,

[15] H. O. L. Fischer and E. Baer, *Helv. Chim. Acta*, 1934, **17**, 622.

J 1·5 Hz, *H*C≡C·CH=), 6·51 [1H, t, *J* 8 Hz, O·CH·C*H*(H)·O], 5·88 [1H, dd, *J* 6 and 8 Hz, O·CH·C*H*(H)·O], 5·05 (1H, qm, *J* 8 Hz, =CH·C*H*(O)·CH_2), 4·48 (1H, dd, *J* 1·5 and 11 Hz, HC≡C·C*H*=CH-*cis*), and 4·00 [1H, dd, *J* 8 and 11 Hz, CH=C*H*·CHO], *m/e* 137 (M^+ − 15, 93%), 122 (80), 107 (65), 95 (74), 94 (22), 93 (25), 79 (50), 78 (25), 77 (35), 72 (70), 65 (50), and 43 (100).

(4S)-2,2-*Dimethyl*-4-(*undec*-cis-1-*ene*-3,5,7-*triynyl*)-1,3-*dioxolan* [*cis*-(X)].—The dioxolan [*cis*-(XVI)] gave in a coupling reaction carried out analogously to that with the *trans*-isomer the chromatographically homogeneous cis-*triynene dioxolan* [*cis*-(X)], $[\alpha]^{20}$ −50 (589 nm), −54 (578), −65 (546), and −164° (436) (*c* 0·312 in EtOH), $\lambda_{max.}$ (EtOH) 332 (ε 10,200), 310 (14,000), 291 (10,800), 274 (6000), 259 (4000), 245·5 (92,500), and 234 (64,200) nm, $\nu_{max.}$ (CCl_4) 2210 and 2180 (C≡C) cm^{-1}, $\nu_{max.}$ (CS_2) 785 (*cis*-CH=CH) cm^{-1}, τ (CCl_4) 8·98 (3H, t, *J* 7 Hz, C*H*$_3$·CH_2), 8·68 (6H, s, CH_3·C·CH_3), 8·41 (2H, sextet, *J* 7 Hz, CH_3·C*H*$_2$·CH_2), 7·79 (2H, t, *J* 7 Hz, CH_2·C*H*$_2$·C≡C), 6·52 [1H, t, *J* 8 Hz, O·CH·C*H*(H)·O], 5·87 [1H, dd, *J* 7 and 8 Hz, O·CH·C*H*(H)·O], 5·08 [1H, qm, *J* 7 Hz, =CH·C*H*(O)·CH_2·O], 4·43 (1H, d, *J* 12 Hz, C≡C·C*H*=CH), and 3·89 (1H, dd, *J* 8 and 12 Hz, ≡C·CH=C*H*·CH), *m/e* 242 (M^+, 7%), 227 (24), 212 (31), 185 (31), 184 (100), 155 (47), 141 (75), 128 (50), 127 (60), 115 (80), 114 (24), 99 (21), and 87 (21).

(2S)-*Tridec*-cis-3-*ene*-5,7,9-*triyne*-1,2-*diol* [*cis*-(II)].—The dioxolan [*cis*-(X)] (40 mg) gave, analogously to the *trans*-isomer, the cis-*diol* [*cis*-(II)] (20 mg) as needles, m.p. 73—74° (Found: C, 77·5; H, 7·0. $C_{13}H_{14}O_2$ requires C, 77·3; H, 7·0%), $[\alpha]^{20}$ −38 (589 nm), −42 (578), −40·5 (546), and −69·5° (436) (*c* 0·253 in EtOH), $\lambda_{max.}$ (EtOH) 326 (ε 12,600), 309 (18,200), 290 (14,000), 273 (7300), 258 (4300), 243 (106,000), and 232 (75,500) nm, $\nu_{max.}$ (CCl_4) 3600 and 3350 (OH) and 2210 (C≡C) cm^{-1}, $\nu_{max.}$ (CS_2) 780 (*cis*-CH=CH) cm^{-1}, τ (CCl_4) 8·92 (3H, t, *J* 7 Hz, C*H*$_3$·CH_2), 8·42 (m, CH_3·C*H*$_2$·CH_2), 7·89br (OH, disappears on addn. of D_2O), 7·70 (2H, t, *J* 7 Hz, CH_2·C*H*$_2$·C≡C), 7·58br (OH, disappears on addn. of D_2O), 6·36 (2H, m, O·CH·C*H*$_2$·O), 5·34 (1H, m, O·C*H*·CH_2·O), 4·38 (1H, dd, *J* 12 and 1 Hz, C≡C·C*H*=CH·CH), and 3·89 (1H, dd, *J* 12 and 8 Hz, CH=C*H*·CH·O).

(2S)-6-*Trimethylsilylhex*-cis-3-*en*-5-*yne*-1,2-*diol* [*cis*-(XVIII)].—The *cis*-dioxolan (XV) (75 mg, 0·34 mmol) was treated with *p*-MeC_6H_4·SO_3H (25 mg) as described for the *trans*-isomer and gave the *cis*-trimethylsilyl diol [*cis*-(XVIII)] (54 mg, 88%), $[\alpha]^{20}$ +19 (589 nm), +20 (578), +22·5 (546), +38 (436), and +56·5° (365) (*c* 0·863 in EtOH), $\lambda_{max.}$ (Et_2O) 244 (ε 11,300) and 234 (13,800) nm, $\nu_{max.}$ (CCl_4) 3600 (OH) and 2150 (C≡C) cm^{-1}, $\nu_{max.}$ (CS_2) 765 (*cis*-CH=CH) cm^{-1}, τ ($CDCl_3$) 9·80 (9H, s, Me_3Si), 7·80br (2H, s, *H*O·CH·CH_2·O*H*; disappears on addn. of D_2O), 6·1—6·45 (2H, m, O·CH·C*H*$_2$·O), 5·1—5·35 [1H, m, CH=CH·C*H*(O)·CH_2], 4·35 (1H, d, *J* 11 Hz, C≡C·C*H*=CH), and 4·04 [1H, dd, *J* 11 and 7 Hz, CH=C*H*·CH(O)], *m/e* 184 (M^+, <1%), 153 (M^+ − CH_2OH, 34), 125 (17), 75 (72), and 73 (100).

1-*Bromohepta*-1,3-*diyne*.—To CuCl (120 mg), NH_2OH,HCl (4·2 g), $EtNH_2$–H_2O (40%, 4·8 ml), and MeOH (10 ml) stirred under N_2 at 20° were added first 3-methylpent-1-yn-3-ol (2·95 g, 30 mmol) in MeOH (30 ml), and then, after 20 min, 1-bromopent-1-yne (4·42 g, 30 mmol) in MeOH (50 ml). After further stirring (2 h), ice (150 g)–H_2O (300 ml)–KCN (1·5 g) was added. The oily residue obtained on Et_2O extraction and concentration was dissolved in EtOH (15 ml) and shaken for 0·5 h in the dark with $AgNO_3$ (500 mg) in EtOH (5 ml)–H_2O (5 ml). The mixture was filtered and the filtrate diluted with H_2O and extracted with Et_2O. The concentrated extract was chromatographed (SiO_2; Et_2O–petrol, 30%) and yielded 3-*methyldeca*-4,6-*diyn*-3-*ol* (2·13 g, 44%), b.p. 80—85° (bath) (Found: C, 79·6; H, 9·9. $C_{11}H_{16}O$ requires C, 80·5; H, 9·9%), $\nu_{max.}$ (CCl_4) 3610 and 3300 (OH) and 2245 (C≡C) cm^{-1}, τ (CCl_4) 8·98 (6H, t, *J* 7 Hz, 2 × C*H*$_3$·CH_2), 8·57 (3H, s, C≡C·C·CH_3), 8·30—8·42 (4H, m, 2 × CH_3·C*H*$_2$), 7·75 (2H, t, *J* 7 Hz, CH_2·C*H*$_2$·C≡C), and 7·37br (1H, s, OH).

The carbinol (1·45 g) and KOH (24 mg) were placed in the distillation flask of a short-path distillation apparatus and plunged at 15 mmHg into an oil-bath kept at 135°. The crude distillate was collected at −78° and gave on chromatography (SiO_2; petrol) hepta-1,3-diyne [16] (0·71 g, 88%), $\nu_{max.}$ (CCl_4) 3320 (C≡C–H) and 2230 (C≡C) cm^{-1}. This in Et_2O (4 ml) was added dropwise to a vigorously stirred solution of NaOBr [from NaOH (6·4 g), Br_2 (3·7 ml), ice (25 g) and H_2O (15 ml)]. After 2 h stirring, Et_2O extraction followed by chromatography (SiO_2; petrol–Et_2O, 4 : 1) gave 1-bromohepta-1,3-diyne (1·25 mg, 95%) as an unstable oil, $\nu_{max.}$ (CCl_4) 2150 (C≡C) cm^{-1}, τ (CCl_4) 8·98 (3H, t, *J* 7 Hz, C*H*$_3$·CH_2), 8·42 (2H, sextet, *J* 7 Hz, CH_3·C*H*$_2$·CH_2), and 7·77 (2H, t, *J* 7 Hz, CH_2·C*H*$_2$·C≡C), which was used directly in the coupling reaction.

Synthesis of Methyl 10-*Hydroxydec*-trans-8-*ene*-4,6-*diynoate* (VI; R = Me) *and Methyl* 9-*Hydroxynon*-trans-7-*ene*-3,5-*diynoate* (VII; R = Me).—The reaction sequence described [6] for the synthesis of the ester (VII; R = Me) was used with modifications which considerably increased the yields. CrO_3 (7·5 g) in conc. H_2SO_4 (15 g) and H_2O (30 ml) was added dropwise to pent-4-yn-1-ol (5·5 g) stirred in H_2O (20 ml)–Me_2CO (30 ml) below 20°. Stirring was continued for 1 h, H_2O was added, and pent-4-yn-1-oic acid was isolated with Et_2O and $NaHCO_3$ and crystallised (CCl_4–petrol); yield 4·1 g (64%); m.p. 60—62° (lit.,[17] 57—58°) (Found: C, 61·0; H, 6·0. Calc. for $C_5H_6O_2$: C, 61·2; H, 6·2%), τ (CCl_4) 8·14 (1H, t, *J* 2·5 Hz, *H*C≡C·CH_2), 7·45br (4H, s, C≡C·CH_2·CH_2·CO), and −1·23 (1H, s, CO_2H; disappears on D_2O addition). This (0·98 g, 10 mmol) in MeOH (5 ml) was added to CuCl (100 mg), NH_2·OH,HCl (1·1 g), and $EtNH_2$ (30% in H_2O; 2·5 ml) stirred in MeOH (5 ml) under N_2 at 0°. After 5 min, 5-bromopent-*trans*-2-en-4-yn-1-ol [6] (1·77 g, 11 mmol) in MeOH (10 ml) was added dropwise and stirring was continued for 2 h. HCl (50 ml; 0·1N) was added and the acids were isolated by Et_2O and $NaHCO_3$ extraction and kept in MeOH–H_2SO_4 (4%, 50 ml) for 24 h. Usual work-up and p.l.c. (petrol–Et_2O, 3 : 1; 4 elutions) gave the C_{10} *ester* (VI; R = Me) (1·23 g, 64%), m.p. *ca.* 15° (Found: M^+, 192·0780. $C_{11}H_{12}O_3$ requires *M*, 192·0786), $\lambda_{max.}$ (EtOH) 282 (ε 16,000), 267 (21,500), 252·5 (15,750), 240 (7500), and 229 (3500) nm, $\nu_{max.}$ (CCl_4) 3620 and 3460 (free and bonded OH), 2240 and 2140 (C≡C), 1740 (ester CO), 1640 (C=C), and 950 (*trans*-CH=CH) cm^{-1}, τ (CCl_4) 8·0br (1H, s, OH; disappears on D_2O addition), 7·4br (4H, s, C≡C·CH_2·CH_2·CO), 6·30 (3H, s, CO_2·CH_3), 5·83 (2H, dd, *J* 2 and 5 Hz, CH=CH·C*H*$_2$·OH), 4·26 (1H, dd, *J* 2 and 16 Hz, C≡C·C*H*=CH·CH_2·OH), and 3·63 (1H, dt, *J* 5 and 16 Hz, CH=C*H*·CH_2·OH), *m/e* 192 (M^+, 87%), 177 (15), 163 (25), 161 (41), 149 (35), 135 (28), 133 (100), 132 (58), 131 (56), 121 (62), 119 (80), 115 (36), 103 (84), 98 (27), 91 (98), 89 (55), 77 (95), 65 (58), 63 (66), and 59 (39).

But-3-ynoic acid [prepared from but-3-yn-1-ol as above in

[16] T. Herbertz, *Chem. Ber.*, 1952, **85**, 475.
[17] G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 1953, 3052.

62% yield, m.p. 82—84° (lit.,[6] 84°), τ (CCl_4) 7·92 (1H, t, *J* 3 Hz, HC≡C), 6·70 (2H, d, *J* 3 Hz, C≡C·CH_2·CO), and −1·0 (1H, s, CO_2H)] (0·84 g, 10 mmol) gave analogously the C_9 ester (VII; R = Me) (1·03 g, 58%), m.p. 55—56° (lit.,[6] 56°), τ (CCl_4) 7·80br (1H, CH_2·O*H*; disappears on D_2O addition), 6·64 (2H, s, C≡C·CH_2·CO), 6·26 (3H, s, CO_2·CH_3), 5·83 (2H, dd, *J* 2 and 5 Hz, CH=CH·CH_2·OH), 4·25 (1H, d, *J* 16 Hz, C≡C·C*H*=CH), and 3·64 (1H, dt, *J* 5 and 16 Hz, CH=C*H*·CH_2·OH), *m/e* 178 (M^+, 31%), 121 (32), 119 (100), 91 (59), 89 (21), 77 (24), 75 (37), 74 (21), and 65 (45).

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