

## Natural Acetylenes. Part XLIV.<sup>1</sup> C<sub>14</sub> Polyacetylenes from *Trachelium caeruleum* L. (Campanulaceae)<sup>2</sup>

By Roger K. Bentley, Cathryn A. Higham, John K. Jenkins, Sir Ewart R. H. Jones,\* and Viktor Thaller, Dyson Perrins Laboratory, Oxford University, Oxford OX1 3QY

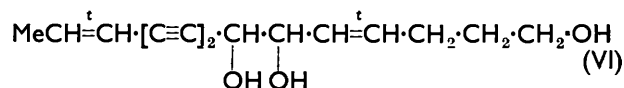
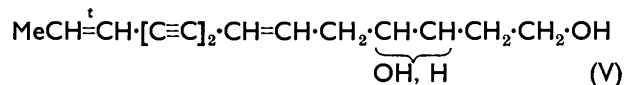
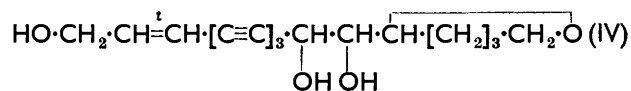
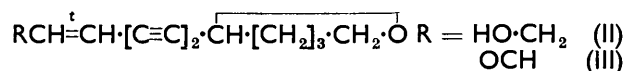
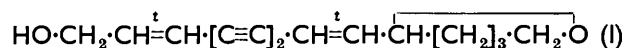
Three new C<sub>14</sub> polyacetylenes, the epoxy-alcohol (R = CH<sub>2</sub>·OH) and aldehyde (R = CHO)

$RCH=CH\cdot[C\equiv C]_2\cdot\overbrace{CH(O)-CH\cdot CH\cdot[CH_2]_3\cdot CH_2\cdot O}$ , and the triol

$HO\cdot CH_2\cdot CH=CH\cdot[C\equiv C]_2\cdot\overbrace{CH(OH)\cdot CH(OH)\cdot CH\cdot[CH_2]_3\cdot CH_2\cdot O}$ , as well as the known alcohol

$HO\cdot CH_2\cdot CH=CH\cdot[C\equiv C]_2\cdot\overbrace{CH=CH\cdot CH\cdot[CH_2]_3\cdot CH_2\cdot O}$  have been detected in extracts from *Trachelium caeruleum* L. A partial structure for another constituent, a C<sub>14</sub> enediynene diol, is proposed. The two epoxides and the triol have been synthesised and their stereochemistry partly elucidated.

THE detection of polyacetylenes in extracts from *Trachelium caeruleum* L. was reported recently.<sup>3</sup> A root extract was analysed subsequently; the known alcohol (I), found already in other members of the Campanulaceae, and the three new polyacetylenes (II)—(IV) were identified; the structure of another, the diol (V), was partly elucidated. The small amount of plant material available prevented a thorough characterisation of the new compounds; however, the spectra (u.v., i.r., and mass) and chemical transformations (Scheme 1) permitted unambiguous allocations of structures, but not of stereochemistry for (II)—(IV).



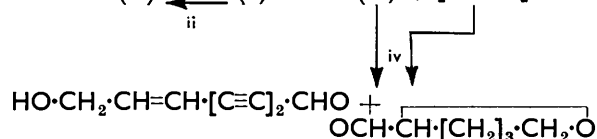
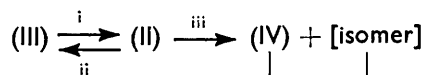
Molecular ions, obtained in the mass spectra of the epoxy-alcohol (II), its acetate, the triol (IV) triacetate,

<sup>1</sup> Part XLIII, M. Ahmed, G. C. Barley, M. T. W. Hearn, Sir Ewart R. H. Jones, V. Thaller, and J. A. Yates, preceding paper.

<sup>2</sup> A more detailed account of part of the work described in this paper is in the D.Phil. Thesis of C. A. Higham, Oxford, 1973.

and the diol (V) diacetate established the molecular formulae of these compounds. The first three all gave a fairly strong peak at *m/e* 85 due to the tetrahydropyranyl group, and transannular epoxide bond fission without hydrogen transfer must account for the abundance of the *m/e* 98 fragment in the spectra of both the epoxy-alcohol (II) and its acetate.

The maxima in the u.v. spectrum of the epoxy-alcohol (II) were those expected for an enediyne epoxide,



SCHEME 1 Reagents: i, NaBH<sub>4</sub>; ii, MnO<sub>2</sub>; iii, H<sub>2</sub>SO<sub>4</sub>-dioxan; iv, NaIO<sub>4</sub>

and changed in the expected fashion on both oxidation and epoxide ring opening. The enediynene diol (V) was not affected by either MnO<sub>2</sub> or periodate treatment: the 1,4-arrangement of the hydroxy-groups is likely on biogenetic grounds [relationship with the triol from *Lobelia cardinalis* (VI)<sup>4</sup>].

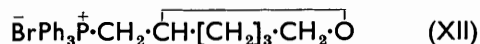
Hydration of the epoxy-alcohol (II) and chromatography gave two closely moving zones with the same u.v. chromophore. The less polar band, the major component, was chromatographically identical with the natural triol (IV). This, as well as the two epoxide (II) hydrolysis products, gave the same fragments on

<sup>3</sup> R. K. Bentley, J. K. Jenkins, Sir Ewart R. H. Jones, and V. Thaller, *J. Chem. Soc. (C)*, 1969, 830.

<sup>4</sup> R. K. Bentley, Sir Ewart R. H. Jones, R. A. M. Ross, and V. Thaller, *J.C.S. Perkin I*, 1973, 140.

periodate treatment (Scheme 1), indicating a *threo-erythro* relationship of the  $\alpha$ -diol system formed on hydration, *i.e.* both *cis*- and *trans*-ring opening of the epoxide occurred.

The structural assignments for the epoxy-alcohol (II), the epoxy-aldehyde (III), and the triol (IV) were confirmed and their stereochemistry was partly elucidated by synthesis (Scheme 2). No indication of the stereochemistry of the epoxy-group being available the synthesis of both the *8-trans*- and the *-cis*-epoxide was carried out. The ylide derived from prop-2-ynylphosphonium salt (VII) and tetrahydropyran-2-carbaldehyde gave the enyne (VIII) in a *trans*:*cis* ratio of 1.4:1 at  $-78^\circ$  and 3:1 at  $0^\circ$  [*cf.* the analogous reaction with 2,3-*O*-isopropylidene-*D*-glyceraldehyde (ref. 1) and references quoted therein)]. The two isomers were separated by chromatography with some *cis*-to-*trans* isomerisation. The carbon-silicon bond cleavage (silver nitrate in ethanol-water<sup>5</sup>) succeeded better with the *trans*- (the silver acetylide separated out in this case) than with the *cis*-isomer. The *cis*-enyne [*cis*-(IX)] was also formed (14% yield) from the phosphonium salt (XII), butyl-lithium, and prop-2-ynal (*cf.* impossibility of obtaining phosphoranes from similar Wittig salts<sup>6</sup>). The *trans*-enyne (IX) was epoxidised readily,



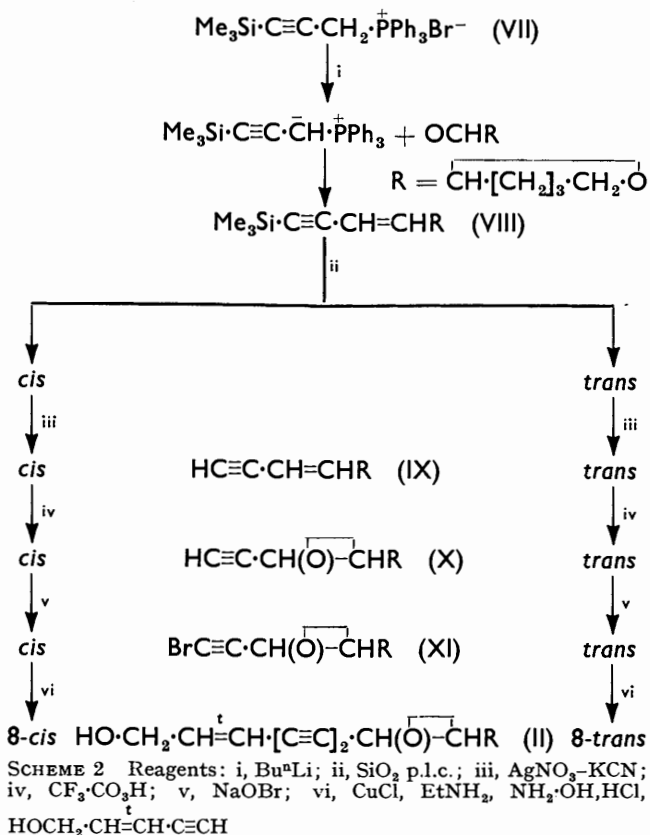
whilst the *cis*-epoxide (X) could be obtained only in poor yield.

On epoxidation of the *trans*-enyne (IX) two compounds were obtained with very slightly differing  $R_F$  values, most likely the two diastereoisomers which can arise on epoxidation of the double bond. The compounds were otherwise identical except for the chemical shifts of the double multiplets allotted to the C(2) proton of the tetrahydropyran ring. In the less polar compound, the signal was centred at  $\tau$  6.07, whereas in the more polar one, it appeared at  $\tau$  6.11. These differences were no longer apparent in the brominated epoxy-acetylene [*trans*-(XI)] and the coupled products.

Coupling of the bromoacetylenes (XI) with *trans*-pentenynol [attempts at coupling the *trans*-epoxy-acetylene (X) under a variety of conditions failed] yielded the two epoxy-alcohols (II) of which the *8-trans*-epoxide and its manganese dioxide oxidation product were identical with the natural alcohol (II) and the aldehyde (III), respectively. This structure allocation has been confirmed by Bohlmann,<sup>7</sup> who also examined *T. caeruleum* and quoted n.m.r. data for the natural epoxy-alcohol (II) which were identical with ours for the synthetic *8-trans*-isomer.

The coupling constants for the epoxide protons in the *trans*-series were 2 Hz and those in the *cis*-series were 4 Hz. Throughout the reaction sequence (Scheme

2) the proton on the tertiary carbon atom of the tetrahydropyran ring gave rise to a double multiplet ( $J$  13 Hz) in all *trans*-1-enes or *trans*-epoxides. In the



*cis*-1-enes, it produced a triple multiplet ( $J$  9 Hz) and in the *cis*-epoxides a double multiplet ( $J$  12 Hz). In both the *trans*- and *cis*-olefins the two protons on C(6) of the tetrahydropyran ring had different chemical shifts, but an easy distinction between the  $\alpha$ - and  $\beta$ -protons was not apparent. Once the double bonds had been epoxidised different chemical shifts for the two protons were no longer observed.

On treating the *trans*-epoxy-alcohol (II) with H<sub>2</sub>SO<sub>4</sub>-dioxan, a mixture of two triols was obtained. The major product (ratio >5:1), by analogy with the transformation of the natural epoxide (II), was the less polar triol, identical with the natural triol (IV). Conversely, when the *cis*-epoxy-alcohol (II) was hydrolysed, the more polar triol (IV) was the major product. Hydration of the *trans*- and *cis*-epoxides, respectively, must therefore have occurred with a similar proportion of *trans*-ring-opening. (The resulting triols were not interconverted under the hydrolysis conditions.) An unequivocal assignment of the *threo*- and *erythro*-configurations to the glycol groups of the hydrolysis

<sup>5</sup> H. M. Schmidt and J. F. Arens, *Rec. Trav. chim.*, 1967, **86**, 1138.

<sup>6</sup> F. Bohlmann and P. Herbst, *Chem. Ber.*, 1959, **92**, 1319.

<sup>7</sup> F. Bohlmann, T. Burkhardt, and C. Zdero, 'Naturally Occurring Acetylenes,' Academic Press, London and New York, 1973, pp. 242 and 487.

products is not possible on the basis of the data available. However, when a mixture of both diastereoisomers is produced on epoxide-hydrolysis, *trans*-ring opening is reported<sup>8</sup> to predominate and the major product obtained from the epoxides (II) could be formed analogously. The natural, less polar triol (IV), should on this basis have the *erythro*-configuration of the  $\alpha$ -diol system.

#### EXPERIMENTAL

For general techniques see Parts XLIII<sup>1</sup> and XXXVI.<sup>4</sup>

1-(*Tetrahydropyran-2-yl*)-4-trimethylsilylbut-1-en-3-yne (VIII).—To (3-trimethylsilylprop-2-ynyl)triphenylphosphonium bromide (VII)<sup>1</sup> (4.54 g, 10 mmol), stirred in  $[\text{CH}_2]_4\text{O}$  (60 ml) under  $\text{N}_2$  at 0° (ice-water cooling), were added dropwise (syringe) first  $\text{Bu}^n\text{Li}$  (12% in hexane; 5 ml, 9.4 mmol) (deep-red colouration) and then, after 0.75 h, tetrahydropyran-2-carbaldehyde<sup>9</sup> (1.14 g, 10 mmol) in  $[\text{CH}_2]_4\text{O}$  (20 ml). Stirring was continued until the red colouration disappeared (1–2 h),  $\text{H}_2\text{O}$  was added (50 ml), and the mixture was extracted with  $\text{Et}_2\text{O}$  ( $3 \times 60$  ml). G.l.c. of the product indicated a *trans*:*cis* ratio of 2.9:1. The  $\text{Et}_2\text{O}$  extract was dried ( $\text{MgSO}_4$ ), concentrated, and passed through a small column ( $\text{SiO}_2$ , 50 g) and the eluate was separated by p.l.c. (petrol- $\text{Et}_2\text{O}$ , 9:1). The band at  $R_F$  0.9 yielded 1-(*tetrahydropyran-2-yl*)-4-trimethylsilylbut-*trans*-1-en-3-yne [*trans*-(VIII)] (1.5 g, 72%),  $t_R$  (121°) 10.3 min (Found:  $M^+$ , 208.1290.  $\text{C}_{12}\text{H}_{20}\text{OSi}$  requires  $M$ , 208.1283),  $\lambda_{\text{max}}$  (EtOH) 246.5 ( $\epsilon$  14,900), 236 (18,950), and 227 (13,100) nm,  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 3020 ( $\text{CH}=\text{CH}$ ), 2137 ( $\text{C}\equiv\text{C}$ ), and 952 (*trans*- $\text{CH}=\text{CH}$ )  $\text{cm}^{-1}$ ,  $\tau$  ( $\text{CCl}_4$ ) 9.84 (s,  $\text{Me}_3\text{Si}$ ), 8.10–8.62 (m,  $\text{CH}[\text{CH}_2]_3\text{CH}_2\text{O}$ ), 6.48–6.77 and 6.06–6.36 (m,  $\text{CH}_2\text{CH}_2\text{O}$ ), 6.07 (dm,  $J$  13 Hz,  $=\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ ), 4.23 (dd,  $J$  16 and 2 Hz,  $\text{C}\equiv\text{C}\cdot\text{CH}=\text{CH}$ ), and 3.98 (dd,  $J$  16 and 4 Hz,  $\text{C}\equiv\text{C}\cdot\text{CH}=\text{CH}$ ),  $m/e$  208 ( $M^+$ , 64%), 165 (34), 137 (29), 135 (54), 109 (29), 83 (38), 75 (74), and 73 (100). The band at  $R_F$  0.8 gave the liquid 1-(*tetrahydropyran-2-yl*)-4-trimethylsilylbut-*cis*-1-en-3-yne [*cis*-(VIII)] (370 mg, 18%);  $t_R$  (121°) 4.6 min,  $\lambda_{\text{max}}$  (EtOH) 246 ( $\epsilon$  13,600), 235.5 (16,550), and 226.5 (11,600) nm,  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 3025 ( $\text{CH}=\text{CH}$ ) and 2150 ( $\text{C}\equiv\text{C}$ )  $\text{cm}^{-1}$ ,  $\nu_{\text{max}}$  ( $\text{CS}_2$ ) 3020 ( $\text{CH}=\text{CH}$ ) and 698 (*cis*- $\text{CH}=\text{CH}$ )  $\text{cm}^{-1}$ ,  $\tau$  ( $\text{CCl}_4$ ) 9.84 (s,  $\text{Me}_3\text{Si}$ ), 8.08–8.62 (m,  $\text{CH}[\text{CH}_2]_3\text{CH}_2\text{O}$ ), 6.75–6.45 (1H, m,  $\text{CH}_2\text{CH}_2\text{O}$ ), 6.10 (1H, dm,  $J$  11 Hz,  $\text{CH}_2\text{CH}_2\text{O}$ ), 5.78 (tm,  $J$  9 Hz,  $=\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ ), 4.66 (d,  $J$  12 Hz,  $\text{C}\equiv\text{C}\cdot\text{CH}=\text{CH}$ ), and 4.15 (dd,  $J$  8 and 12 Hz,  $\text{CH}=\text{CH}\cdot\text{CH}$ ),  $m/e$  208 ( $M^+$ , 2%), 191 (20), 150 (16), 136 (19), 135 (100), 75 (15), and 73 (30).

The experiment was repeated at  $-78^\circ$  ( $\text{Me}_2\text{CO}-\text{CO}_2$  cooling) and gave the reaction product in a 60% yield. The *trans*:*cis* ratio was 1.4:1.

1-(*Tetrahydropyran-2-yl*)-but-*trans*-1-en-3-yne [*trans*-(IX)].— $\text{AgNO}_3$  (540 mg; 3.30 mmol) in  $\text{H}_2\text{O}$  (10 ml) was added dropwise to the trimethylsilyl enyne [*trans*-(VIII)] (243 mg, 1.12 mmol) stirred in EtOH (30 ml) under  $\text{N}_2$  in the dark at 0° (ice-water cooling). Stirring was continued for 0.5 h, the liquid was decanted, and the white Ag salt was dissolved in  $\text{CH}_2\text{Cl}_2$  (40 ml) and poured into KCN (1 g) in  $\text{H}_2\text{O}$  (20 ml). The layers were separated, the  $\text{H}_2\text{O}$  layer was extracted with  $\text{Et}_2\text{O}$  ( $3 \times 20$  ml), and the combined organic layers were washed, dried ( $\text{MgSO}_4$ ), concentrated, and separated by p.l.c. (petrol- $\text{Et}_2\text{O}$ , 9:1). The band at  $R_F$  0.65 gave 1-(*tetrahydropyran-2-yl*)-but-*trans*-1-en-

3-yne<sup>3</sup> [*trans*-(IX)] (110 mg, 72.5%),  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 3308 ( $\text{HC}\equiv\text{C}$ ) and 955 (*trans*- $\text{CH}=\text{CH}$ )  $\text{cm}^{-1}$ ,  $\tau$  ( $\text{CCl}_4$ ) 8.02–8.65 (m,  $\text{CH}[\text{CH}_2]_3\text{CH}_2\text{O}$ ), 7.32 (d,  $J$  2 Hz,  $\text{HC}\equiv\text{C}\cdot\text{CH}$ ), 6.74–6.44 and 6.36–6.06 (m,  $\text{CH}_2\text{CH}_2\text{O}$ ), 6.06 (dm,  $J$  13 Hz,  $=\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ ), 4.44 (ddd,  $J$  17, 2, and 2 Hz,  $\text{HC}\equiv\text{C}\cdot\text{CH}=\text{CH}$ ), and 3.92 (dd,  $J$  17 and 4 Hz,  $\text{CH}=\text{CH}\cdot\text{CH}$ ).

*trans*-3,4-Epoxy-4-(*tetrahydropyran-2-yl*)-but-1-yne [*trans*-(X)].—A solution of  $\text{CF}_3\cdot\text{CO}_3\text{H}$  [from  $(\text{CF}_3\cdot\text{CO})_2\text{O}$  (5.1 ml), in  $\text{CH}_2\text{Cl}_2$  (30 ml), and  $\text{H}_2\text{O}_2$  (90%; 0.84 ml)] was added dropwise over 15 min to the enyne [*trans*-(IX)] (276 mg, 2.0 mmol) and anh.  $\text{Na}_2\text{HPO}_3$  (15 g) stirred in dry  $\text{CH}_2\text{Cl}_2$  (40 ml) at 0° (ice-water cooling). The mixture was then allowed to reach 20° (1 h) and stirring was continued for a further 1 h.  $\text{H}_2\text{O}$  (100 ml) was added, the layers were separated, and the organic layer was dried ( $\text{MgSO}_4$ ), concentrated, and purified by p.l.c. (petrol- $\text{Et}_2\text{O}$ , 9:1). Bands at  $R_F$  0.25 and 0.20 yielded the two diastereoisomers of the *trans*-3,4-epoxy-4-(*tetrahydropyran-2-yl*)-but-1-yne [*trans*-(X)] (204 mg, 66%),  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 3320 ( $\text{HC}\equiv\text{C}$ ) and 2128 ( $\text{C}\equiv\text{C}$ )  $\text{cm}^{-1}$ ,  $\tau$  ( $\text{CCl}_4$ ) 8.10–8.65 (m,  $\text{CH}[\text{CH}_2]_3\text{CH}_2\text{O}$ ), 7.84 (d,  $J$  2 Hz,  $\text{HC}\equiv\text{C}\cdot\text{CH}$ ), 7.11 [dd,  $J$  4 and 2 Hz,  $(\text{O})\text{CH}\cdot\text{CH}\cdot\text{CH}$ ], 6.87 [dd,  $J$  2 and 2 Hz,  $\text{HC}\equiv\text{C}\cdot\text{CH}\cdot\text{CH}(\text{O})$ ], 6.6–7.1 (m,  $\text{CH}_2\text{CH}_2\text{O}$ ), 6.11 (less polar compound; 50 mg) (dm,  $J$  13 Hz,  $>\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ ), and 6.07 (more polar compound; 154 mg) (dm,  $J$  13 Hz,  $>\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ ),  $m/e$  98 (100%), 85 (77), 83 (32), 70 (19), 69 (15), and 67 (25).

The next two stages were first tried on each isomer separately. As neither the bromination nor the coupling products could be distinguished by their spectral and chromatographic properties, the synthesis was carried out on the unresolved mixture.

1-Bromo-*trans*-3,4-epoxy-4-(*tetrahydropyran-2-yl*)-but-1-yne [*trans*-(XI)].— $\text{NaOBr}$  [3 ml; prepared from  $\text{Br}_2$  (11 ml),  $\text{H}_2\text{O}$  (50 ml), ice (100 g), and  $\text{NaOH}$  (20 g)] was added dropwise to the ethynyl epoxide [*trans*-(X)] (204 mg, 1.33 mmol) in  $\text{Et}_2\text{O}$  (1 ml), and the mixture was shaken vigorously for 5 h. Saturated  $\text{NH}_4\text{Cl}$  solution (1 ml) and  $\text{Et}_2\text{O}$  (5 ml) were added to the mixture, and the layers were separated. The  $\text{H}_2\text{O}$  layer was extracted with  $\text{Et}_2\text{O}$  ( $2 \times 5$  ml) and the combined organic layers were washed with  $\text{H}_2\text{O}$  and dried ( $\text{MgSO}_4$ ). The pale yellow solution yielded on concentration 1-bromo-*trans*-3,4-epoxy-4-(*tetrahydropyran-2-yl*)-but-1-yne [*trans*-(XI)] (237 mg, 78%),  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 2220 ( $\text{C}\equiv\text{C}$ )  $\text{cm}^{-1}$ ,  $\tau$  ( $\text{CCl}_4$ ) 8.10–8.72 (m,  $\text{CH}[\text{CH}_2]_3\text{CH}_2\text{O}$ ), 6.55–7.12 (m,  $(\text{O})\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_3\text{CH}_2\text{O}$ ), and 6.07 [dm,  $J$  13 Hz,  $(\text{O})\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ ].

*trans*-8,9-Epoxy-9-(*tetrahydropyran-2-yl*)-*non-trans*-2-ene-4,6-diyn-1-ol (II).—Pent-*trans*-2-en-4-yn-1-ol (82 mg, 1 mmol) in MeOH (3 ml) was added dropwise to  $\text{CuCl}$  (15 mg),  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (180 mg), and  $\text{EtNH}_2$  (40%; 1 ml) in MeOH (2 ml) stirred under  $\text{N}_2$  at 20°. A deep orange precipitate formed. After 5 min, the bromoethynyl epoxide [*trans*-(XI)] (231 mg, 1 mmol) in MeOH (3 ml) was added dropwise. After 3 h KCN,  $\text{Et}_2\text{O}$ , and  $\text{NH}_4\text{Cl}-\text{H}_2\text{O}$  were added and the products were isolated *via*  $\text{Et}_2\text{O}$  and separated by p.l.c. ( $\text{Et}_2\text{O}$ ). The band with  $R_F$  0.85 was further purified by continuous elution (petrol- $\text{Et}_2\text{O}$ , 9:1; 24 h) and the band at  $R_F$  0.2 yielded *trans*-8,9-epoxy-9-(*tetrahydropyran-2-yl*)-*non-trans*-2-ene-4,6-diyn-1-ol (II) (174 mg, 75%) (Found:  $M^+$ , 232.1096.  $\text{C}_{14}\text{H}_{16}\text{O}_3$  requires  $M$ , 232.1099),  $\lambda_{\text{max}}$  (EtOH) 288 ( $\epsilon$  9350), 271.5 (12,525), 256.5 (8900), 244

<sup>3</sup> R. E. Parker, *Chem. Rev.*, 1959, **59**, 737.

<sup>4</sup> J. Colonge and P. Jeltsch, *Bull. Soc. chim. France*, 1963, 1288.

(4500), 215 (77,650), and 2091inf (76,800) nm,  $\nu_{\max}$  (CCl<sub>4</sub>) 3630 and 3470 (OH), 3030 (CH=CH), 2235 (C≡C), and 948 (*trans*-CH=CH) cm<sup>-1</sup>,  $\tau$  (CCl<sub>4</sub>) 8.06—8.61 (m, CH·[CH<sub>2</sub>]<sub>3</sub>·CH<sub>2</sub>·O), 7.78br (OH), 6.97 [dd, *J* 2 and 4 Hz, (O)CH·CH·CH], 6.65—6.85 (m, CH<sub>2</sub>·CH<sub>2</sub>·O), 6.64 [d, *J* 2 Hz, C≡C·CH·CH(O)], 6.08 [dm, *J* 13 Hz, (O)CH·CH·CH<sub>2</sub>], 5.81 (dd, *J* 2 and 4 Hz, CH=CH·CH<sub>2</sub>·OH), 4.25 (dd, *J* 17 and 2 Hz, CH·[C≡C]<sub>2</sub>·CH=CH), and 3.63 (dt, *J* 17 and 4 Hz, CH=CH·CH<sub>2</sub>·OH), *m/e* 232 (*M*<sup>+</sup>, 16%), 98 (92), 90 (73), 89 (100), 85 (53), and 74 (36).

1-(Tetrahydropyran-2-yl)but-cis-1-en-3-yne [*cis*-(IX)].—(a) AgNO<sub>3</sub> (540 mg; 3.30 mmol) in H<sub>2</sub>O (10 ml) was added dropwise to the trimethylsilyl enyne [*cis*-(VIII)] (243 mg, 1.12 mmol) stirred in EtOH (20 ml) under N<sub>2</sub> in the dark at 0° (ice-water cooling). The yellow mixture was poured after 0.5 h into H<sub>2</sub>O (100 ml)—KCN (1 g). Extraction with Et<sub>2</sub>O and p.l.c. (petrol—Et<sub>2</sub>O, 9:1) of the concentrated extract gave a band (*R*<sub>F</sub> 0.55) which yielded 1-(tetrahydropyran-2-yl)but-cis-1-en-3-yne [*cis*-(IX)] (92 mg, 58%) (Found: *M*<sup>+</sup>, 136.0889. C<sub>9</sub>H<sub>12</sub>O requires *M*, 136.0888),  $\nu_{\max}$  (CCl<sub>4</sub>) 3316 (HC≡C), 3034 (CH=CH), and 2098 (C≡C) cm<sup>-1</sup>,  $\nu_{\max}$  (CS<sub>2</sub>) 3312 (HC≡C), 3030 (CH=CH), and 738 (*cis*-CH=CH) cm<sup>-1</sup>,  $\tau$  (CCl<sub>4</sub>) 8.07—8.62 (m, CH·[CH<sub>2</sub>]<sub>3</sub>·CH<sub>2</sub>·O), 7.00 (d, *J* 2 Hz, HC≡C·CH), 6.74—6.45 (1H, m, CH<sub>2</sub>·CH<sub>2</sub>·O), 6.10 (1H, dm, *J* 11 Hz, CH<sub>2</sub>·CH<sub>2</sub>·O), 5.78 (tm, *J* 9 Hz, =CH·CH·CH<sub>2</sub>), 4.63 (ddd, *J* 11, 4, and 2 Hz, HC≡C·CH=CH), and 4.09 (dd, *J* 11 and 8 Hz, CH=CH·CH) [on irradiation at  $\tau$  4.09 (vinylic proton) the signal at  $\tau$  5.78 collapsed to a double multiplet, whilst the multiplets centred at  $\tau$  6.1 and 6.6 remained unchanged], *m/e* 136 (*M*<sup>+</sup>, 96%), 135 (66), 94 (67), 91 (91), 85 (87), 79 (100), 78 (73), and 77 (70).

(b) Bu<sup>n</sup>Li (12% in hexane; 0.5 ml, 0.9 mmol) was added dropwise to the Wittig salt (XII) (m.p. 238—240°; <sup>10</sup> 441 mg, 1 mmol) in [CH<sub>2</sub>]<sub>4</sub>O (10 ml) stirred under N<sub>2</sub> at 0° (ice-water cooling). After 5 min, prop-2-ynal (54 mg, 1 mmol) in Et<sub>2</sub>O (1 ml) was added and the mixture was stirred at 20° for 0.5 h. HCl (2*N*; 5 ml) was added, the layers were separated and the organic layer was dried (MgSO<sub>4</sub>) and concentrated. P.l.c. (petrol—Et<sub>2</sub>O, 9:1) gave a band at *R*<sub>F</sub> 0.55 which yielded the enyne [*cis*-(IX)] (19 mg, 14%).

*cis*-3,4-Epoxy-4-(tetrahydropyran-2-yl)but-1-yne [*cis*-(X)].—A solution of CF<sub>3</sub>·CO<sub>3</sub>H [from (CF<sub>3</sub>·CO)<sub>2</sub>O (1.7 ml) and H<sub>2</sub>O<sub>2</sub> (0.28 ml) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml)] was added dropwise over 5 min to the enyne [*cis*-(IX)] (92 mg, 0.67 mmol) and anh. Na<sub>2</sub>HPO<sub>3</sub> (5 g) stirred in dry CH<sub>2</sub>Cl<sub>2</sub> (20 ml) at 0° (ice-water cooling). The isolated product (see above) was purified by p.l.c. (petrol—Et<sub>2</sub>O, 9:1). The band at *R*<sub>F</sub> 0.20 gave *cis*-3,4-epoxy-4-(tetrahydropyran-2-yl)but-1-yne [*cis*-(X)] (23 mg, 22%),  $\nu_{\max}$  (CCl<sub>4</sub>) 3318 (HC≡C) and 2122 (C≡C) cm<sup>-1</sup>,  $\tau$  (CCl<sub>4</sub>) 8.05—8.63 (m, CH·[CH<sub>2</sub>]<sub>3</sub>·CH<sub>2</sub>·O), 7.73 (d, *J* 2 Hz, HC≡C·CH), 7.10 [dd, *J* 4 and 8 Hz, (O)CH·CH·CH], 6.66 [dd, *J* 2 and 4 Hz, HC≡C·CH·CH(O)], 6.38—6.90 (m, CH<sub>2</sub>·CH<sub>2</sub>·O), and 5.98 [dm, *J* 12 Hz, (O)CH·CH·CH<sub>2</sub>].

1-Bromo-*cis*-3,4-epoxy-4-(tetrahydropyran-2-yl)but-1-yne [*cis*-(XI)].—The ethynyl epoxide [*cis*-(X)] (23 mg) in Et<sub>2</sub>O (1 ml) and NaOBr (2 ml; prepared as above) were shaken vigorously for 5 h. Work-up as for the *trans*-isomer gave 1-bromo-*cis*-3,4-epoxy-4-(tetrahydropyran-2-yl)but-1-yne [*cis*-(XI)] (25.2 mg, 72%),  $\nu_{\max}$  (CCl<sub>4</sub>) 2212 (C≡C) cm<sup>-1</sup>,  $\tau$  (CCl<sub>4</sub>)

8.07—8.67 (m, CH·[CH<sub>2</sub>]<sub>3</sub>·CH<sub>2</sub>·O), 7.20 [dd, *J* 4 and 8 Hz, (O)CH·CH·CH], 6.40—7.02 (m, CH<sub>2</sub>·CH<sub>2</sub>·O), 6.73 [d, *J* 4 Hz, C≡C·CH·CH(O)], and 6.09 [dm, *J* 12 Hz, (O)CH·CH·CH<sub>2</sub>].

*cis*-8,9-Epoxy-9-(tetrahydropyran-2-yl)non-*trans*-2-ene-4,6-diyn-1-ol [*cis*-(II)].—To CuCl (2.5 mg), NH<sub>2</sub>OH.HCl (20 mg), and EtNH<sub>2</sub> (40%, 0.2 ml) stirred in MeOH (0.5 ml) under N<sub>2</sub> at 20° was added dropwise pent-*trans*-2-ene-4-yn-1-ol (8.2 mg, 0.1 mmol) in MeOH (1 ml) followed, after 5 min, by the bromoethynyl epoxide [*cis*-(XI)] (23.1 mg, 0.1 mmol) in MeOH (2 ml). The mixture was worked up after 3 h and purified as in the experiment with the *trans*-isomer to yield *cis*-8,9-epoxy-9-(tetrahydropyran-2-yl)non-*trans*-2-ene-4,6-diyn-1-ol [*cis*-(II)] (18.6 mg, 80%) (Found: *M*<sup>+</sup>, 232.1096. C<sub>14</sub>H<sub>16</sub>O<sub>3</sub> requires *M*, 232.1099),  $\lambda_{\max}$  (EtOH) 289 ( $\epsilon$  7400), 273 (10,550), 258 (7300), 245 (3700), 217 (33,700), and 211.5inf (32,250) nm,  $\nu_{\max}$  (CCl<sub>4</sub>) 3620 (OH), 3020 (CH=CH), 2230 (C≡C), and 950 (*trans*-CH=CH) cm<sup>-1</sup>,  $\tau$  (CCl<sub>4</sub>) 8.05—8.70 (m, CH·[CH<sub>2</sub>]<sub>3</sub>·CH<sub>2</sub>·O), 7.09 [dd, *J* 4 and 8 Hz, (O)CH·CH·CH], 6.40—6.95 (m, CH<sub>2</sub>·CH<sub>2</sub>·O), 6.59 [d, *J* 4 Hz, C≡C·CH·CH(O)], 6.01 [dm, *J* 12 Hz, (O)CH·CH·CH<sub>2</sub>], 5.79 (dd, *J* 2 and 4 Hz, CH=CH·CH<sub>2</sub>·OH), 5.16br (OH), 4.22 (dd, *J* 17 and 2 Hz, CH·[C≡C]<sub>2</sub>·CH=CH), and 3.58 (dt, *J* 17 and 4 Hz, CH=CH·CH<sub>2</sub>·OH), *m/e* 232 (*M*<sup>+</sup>, 3%), 98 (61), 91 (18), 90 (38), 89 (100), 85 (29), and 69 (19).

*trans*-8,9-Epoxy-9-(tetrahydropyran-2-yl)non-2-ene-4,6-diynal (III).—The alcohol (II) (46.4 mg, 0.2 mmol) was shaken with MnO<sub>2</sub> (464 mg) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) for 0.5 h. Filtration (Celite), concentration, and p.l.c. (petrol—Et<sub>2</sub>O, 4:1) gave quantitatively *trans*-8,9-epoxy-9-(tetrahydropyran-2-yl)non-2-ene-4,6-diynal (III), an unstable oil (Found: *M*<sup>+</sup>, 230.0943. C<sub>14</sub>H<sub>14</sub>O<sub>3</sub> requires *M*, 230.0943),  $\lambda_{\max}$  (Et<sub>2</sub>O) 308 (rel. *E* 0.91), 289.5 (1.0), 273 (0.51), and 257.5 (0.19) nm,  $\nu_{\max}$  (CCl<sub>4</sub>) 3038 (CH=CH), 2720 (CHO), 2228 and 2148 (C≡C), 1696 (C=O), and 956 (*trans*-CH=CH) cm<sup>-1</sup>,  $\tau$  (CCl<sub>4</sub>) 8.10—8.69 (m, CH·[CH<sub>2</sub>]<sub>3</sub>·CH<sub>2</sub>·O), 6.92 [dd, *J* 2 and 4 Hz, (O)CH·CH·CH], 6.60—6.85 (m, CH<sub>2</sub>·CH<sub>2</sub>·O), 6.60 [d, *J* 2 Hz, C≡C·CH·CH(O)], 6.07 [dm, *J* 13 Hz, CH·CH·CH<sub>2</sub>], 3.40—3.50 (m, CH·[C≡C]<sub>2</sub>·CH=CH·CHO), and 0.45 (dd, *J* 4 and 3 Hz, CH=CH·CHO), *m/e* 230 (*M*<sup>+</sup>, 2%), 116 (40), 98 (100), 88 (48), 87 (25), 85 (26), and 62 (30).

9-(Tetrahydropyran-2-yl)non-2-ene-4,6-diyn-1,8,9-triol (IV).—The alcohol (II) (46.4 mg, 0.2 mmol) in dioxan (5 ml)—H<sub>2</sub>SO<sub>4</sub> (*M*, 0.5 ml), was kept at 65° for 15 min. The mixture was concentrated, the products were isolated with Et<sub>2</sub>O (3 × 10 ml), and the combined extracts were dried (MgSO<sub>4</sub>), concentrated, and subjected to p.l.c. (Et<sub>2</sub>O—MeOH, 97:3). The band at *R*<sub>F</sub> 0.5 yielded erythro-8,9-(tetrahydropyran-2-yl)non-2-ene-4,6-diyn-1,8,9-triol (IV) (40 mg) (Found: *M*<sup>+</sup>, 250.1209. C<sub>14</sub>H<sub>18</sub>O<sub>4</sub> requires *M*, 250.1205),  $\lambda_{\max}$  (EtOH) 284 ( $\epsilon$  9900), 263.5 (13,200), 254 (8700), 241.5 (3900), 230 (1800), 215.5 (66,800), and 208 (48,900) nm,  $\nu_{\max}$  (CHCl<sub>3</sub>) 3560 and 3410 (OH), 2228 (C≡C), and 950 (*trans*-CH=CH) cm<sup>-1</sup>,  $\tau$  (CDCl<sub>3</sub>) 8.10—8.60 (m, CH·[CH<sub>2</sub>]<sub>3</sub>·CH<sub>2</sub>·O), 5.95—6.65 {m, 3 × OH and CH(OH)·CH(OH)·CH·[CH<sub>2</sub>]<sub>3</sub>·CH<sub>2</sub>·O}, 5.77 (d, *J* 4 Hz, =CH·CH<sub>2</sub>·OH), 4.20 (d, *J* 17 Hz, CH=CH·CH<sub>2</sub>·OH), and 3.56 (dt, *J* 17 and 4 Hz, CH=CH·CH<sub>2</sub>·OH), *m/e* 250 (*M*<sup>+</sup>, 2%), 118 (100), 115 (35), 97 (18), 85 (25), 77 (24), and 119 (14).

A closely running (*R*<sub>F</sub> 0.4) minor band yielded the *threo*-triol (IV) (4 mg). The combined yield was 88%.

<sup>10</sup> M. J. Wright, D.Phil. Thesis, Oxford, 1970.

When the *cis*-epoxy-alcohol [*cis*-(II)] (*ca.* 2 mg) was treated analogously with dioxan-H<sub>2</sub>SO<sub>4</sub> the major spot obtained by t.l.c. had  $R_F$  0.4 and the minor one  $R_F$  0.5.

*Isolation of Polyacetylenes.*—Minced roots (300 g) of *Trachelium caeruleum* L. from twelve plants, grown indoors and harvested before flowering, were extracted with Et<sub>2</sub>O. The concentrated extracts were chromatographed on a SiO<sub>2</sub> column (200 × 35 mm) from Et<sub>2</sub>O. Three groups of fractions were collected and combined: (i) non-polar material which was not retained on the column, (ii) material of intermediate polarity eluted with Et<sub>2</sub>O, and (iii) polar material eluted with Et<sub>2</sub>O-MeOH (9 : 1).

Rechromatography of the least polar fraction on 1 mm layers (first CH<sub>2</sub>Cl<sub>2</sub> and then petrol-Et<sub>2</sub>O, 1 : 1) gave the epoxy-aldehyde (III) (3 mg),  $\lambda_{\max}$  308 (rel. *E* 0.9), 290 (1.0), 273 (0.65), and 258 (0.42) nm,  $\nu_{\max}$  (CHCl<sub>3</sub>) 1690 (CHO) cm<sup>-1</sup>, and a more polar zone,  $\lambda_{\max}$  312, 293, and 276 nm, containing a large amount of non-acetylenic material which prevented further purification of the polyacetylene. The chromophore of the latter was not affected by either MnO<sub>2</sub> or NaBH<sub>4</sub>.

Rechromatography of the intermediate polarity fraction on SiO<sub>2</sub> layers (first Et<sub>2</sub>O and then CHCl<sub>3</sub>; continuous elution) gave 9-(tetrahydropyran-2-yl)nona-2,8-diene-4,6-diyn-1-ol (I) <sup>3</sup> (8 mg) and the slightly more polar epoxy-alcohol (II) (10 mg),  $\lambda_{\max}$  288 (rel. *E* 0.75), 272 (1.0), 257 (0.6), and 244 (0.3) nm,  $\nu_{\max}$  (CHCl<sub>3</sub>) 3595, 3400 (OH), 2225 (C=C), 1090 (tetrahydropyran), and 875 (epoxide) cm<sup>-1</sup>, *m/e* 232 (*M*<sup>+</sup>, 24%), 118 (27), 98 (92), 90 (45), 89 (100), and 85 (51); the corresponding acetate had *m/e* 274 (*M*<sup>+</sup>, 20%), 149 (26), 117 (100), 98 (87), 90 (26), 85 (70), and 43 (95).

The most polar fraction gave on chromatography (first Et<sub>2</sub>O-MeOH, 97 : 3, then CHCl<sub>3</sub>-MeOH, 9 : 1) a diol of partial structure (V) (3 mg),  $\lambda_{\max}$  312 (rel. *E* 0.75), 293 (1.0), and 276 (0.75) nm, which was not affected by either MnO<sub>2</sub> or NaIO<sub>4</sub> and gave an acetate, *m/e* 302 (*M*<sup>+</sup>, 27%), 259 (*M*<sup>+</sup> - CH<sub>3</sub>CO, 23), 242 (*M*<sup>+</sup> - CH<sub>3</sub>CO<sub>2</sub>H, 6), 201 [*M*<sup>+</sup> - (CH<sub>3</sub>CO + CH<sub>3</sub>CO<sub>2</sub>H), 100], 199 (41), 171 (30),

159 (32), 145 (47), and 115 (70), and the more polar triol (IV) (5 mg),  $\lambda_{\max}$  283 (rel. *E* 0.8), 267 (1.0), 253 (0.6), and 240 (0.4) nm, the acetate of which had *m/e* 376 (*M*<sup>+</sup>, 14%) and 85 (100%).

*Reduction of the Aldehyde* (III).—An Et<sub>2</sub>O solution of the aldehyde (III) was stirred with an excess of NaBH<sub>4</sub> for 2 h. The product was purified by t.l.c. (petrol-Et<sub>2</sub>O, 1 : 2) and had u.v. and mass spectra as well as  $R_F$  values identical with those of the alcohol (II).

*Oxidation of the Alcohol* (II).—An Et<sub>2</sub>O solution (10 ml) of the alcohol (II) was shaken with MnO<sub>2</sub> (20 mg) until no further change in u.v. absorption occurred. The oxidation product was identical in t.l.c. behaviour and u.v. spectrum with the aldehyde (III); it changed its chromophore when dissolved in MeOH-H<sub>2</sub>SO<sub>4</sub> [to  $\lambda_{\max}$  288 (rel. *E* 0.85), 272 (1.0), 257 (0.65), and 244 (0.25) nm].

*Hydration of the Epoxy-alcohol* (II).—A solution of the epoxy-alcohol (II) (3 mg) in dioxan (1 ml) containing H<sub>2</sub>SO<sub>4</sub> (m; 2 drops) was kept at 65° for 15 min, the products were transferred into Et<sub>2</sub>O and the solution was dried (K<sub>2</sub>CO<sub>3</sub>), and yielded on chromatography (Et<sub>2</sub>O-MeOH, 97 : 3) two closely moving zones, both with  $\lambda_{\max}$  283 (rel. *E* 0.8), 267 (1.0), 253 (0.6), and 240 (0.25) nm. The less polar, major product, and the triol (IV) had identical  $R_F$  values. Both the major and minor product gave the same periodate fission products as the triol (IV).

*Periodate Cleavage of the Triol* (IV).—The triol (IV) (2 mg) in Et<sub>2</sub>O (5 ml) was shaken for 2 h with NaIO<sub>4</sub> in H<sub>2</sub>O (5 ml). The organic layer then had  $\lambda_{\max}$  318 (rel. *E* 0.85), 300 (1.0), 283 (0.85), and 267 (0.65) nm (*cf.*  $\lambda_{\max}$  for oct-6-ene-2,4-diynal<sup>4</sup>); a major component of the mixture had  $t_R$  (70°) 8.5 min, identical with that of authentic tetrahydropyran-2-carbaldehyde.

We thank the National Research Council of Canada for a fellowship (J. K. J.) and the S.R.C. for a studentship (C. A. H.) and research support.

[4/505 Received, 14th March 1974]