Medicinal Plants of Southern Africa. Part 2.[1] Synthesis of 1,3-Bis-(4-methoxyphenyl)penta-1,4-diene, a Stereoisomer of Dimethylhinokiresinol, and its 4-Monomethoxy Analogue

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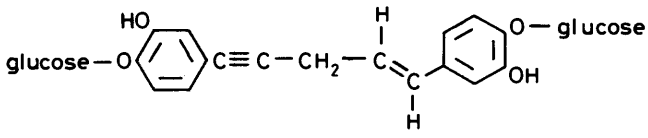
A six-step synthesis of the title compounds (**6**) and (**7**) from prop-2-yn-1-ol, and proceeding *via* 3-(4-methoxyphenyl)prop-1-yne, is described. Detailed ^{1}H n.m.r. spectral analysis (500 MHz) suggests that the synthetic compounds have a 1,2-*E* stereochemistry in contrast to the *Z*-configuration present in the naturally occurring hinokiresinol (**3**). By utilizing a different, and much less efficient route, a small quantity of (*Z*)-3-(4-methoxyphenyl)-1-phenylpenta-1,4-diene (**5**) was obtained.

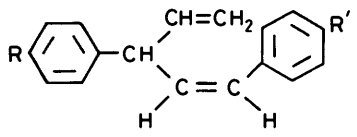
Extracts from plants of the genus *Hypoxis* have found a variety of uses in African traditional medicine. Afflictions that have been treated include urinary infections, internal parasites, and abdominal pains.[2] There is considerable current interest in the extracts from Hypoxidaceae on account of their reported activity as antibacterial agents,[3,4] as well as their activity against lymphocytic leukaemia.[5] Marini-Bettolo *et al.*[6,7] have recently isolated two glucosides from *Hypoxis* spp. and suggested the trivial names hypoxoside (**1**) and nyasoside (**2**). A synthesis of the tetramethoxy derivative of the aglucone of (**1**) has been reported by us.[8] Hypoxoside (**1**) is the first natural product possessing the novel pent-1-en-4-yne system. Nyasoside (**2**) may be regarded as a 3-aryl-substituted penta-1,4-diene, possibly derived from the above pentenyne system. It is of interest to note that the polyacetylenic alcohol obtained from the marine sponges *Tetrosia* spp. has the related functionality -C≡CCH-(OH)CH=CH- along its chain. This substance has the property of inhibiting cell division of fertilized sea urchin eggs.[9]

Marini-Bettolo[7] has assigned the name nyasol to the aglucone (**3**) of nyasoside. No mention was made of the fact that the identical compound, named hinokiresinol, was isolated for the first time by Hirose *et al.*[10] from the heartwood of *Chamaecyparis obtusa* in 1965. Hirose *et al.* regard hinokiresinol as being one of a class of 1,3-diarylpentane derivatives related biogenetically to lignans with a C_{17} skeleton. In these circumstances we will use the term hinokiresinol.

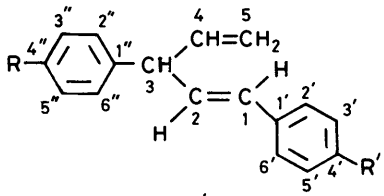
In this communication the emphasis is on (i) the novel synthesis of (*E*)-1,3-bis-(4-methoxyphenyl)penta-1,4-diene (**6**) and its mono(4-methoxyphenyl) analogue (**7**), and (ii) a detailed ^{1}H n.m.r. analysis of the monomethoxy analogue (**7**). This was considered important since previous analysis of the ABX and the KPQX systems present in these compounds have been very superficial.



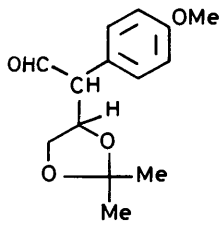
(**1**)



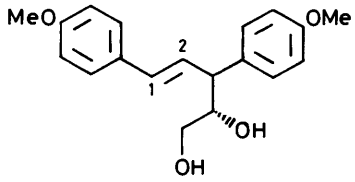
(**2**) R = R′ = O—Glucose
(**3**) R = R′ = OH
(**4**) R = R′ = OMe
(**5**) R = OMe, R′ = H



(**6**) R = R′ = OMe
(**7**) R = OMe, R′ = H



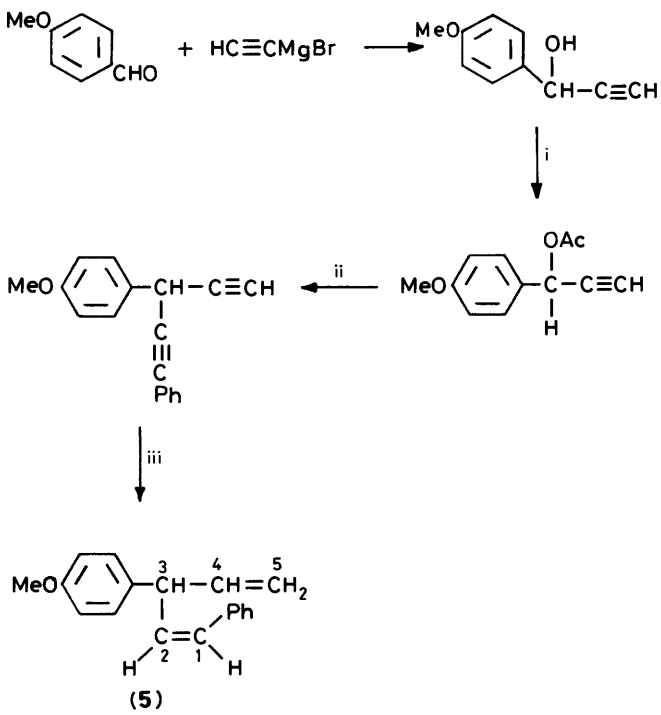
(**8**)



(**9**)

Earlier Synthesis of the 4,4′-Dimethoxy Ether of Hinokiresinol (**4**).—In 1979 Whiting and Beracierta[11] synthesized compound (**4**) from the key intermediate (**8**), an arylacetaldehyde. This aldehyde was obtained in eight steps through transformation of 4-methoxyacetophenone. The synthesis described by these authors is a versatile one since the dioxolane (**8**) could also be used for conversion into other norlignans such as agatharesinol and sequirin A. In order to obtain the target molecule from compound (**8**) an additional four steps were required.

Synthesis of (Z)-3-(4-*Methoxyphenyl*)-1-*phenylpenta*-1,4-*diene* (**5**).—This synthesis (Scheme 1), termed the 'acetate synthesis', involved reaction of 4-methoxybenzaldehyde with ethynylmagnesium bromide, acetylation of the resultant secondary alcohol, and subsequent *nucleophilic* displacement of the acetyl group with phenylacetylide to afford 3-(4-methoxyphenyl)-1-phenylpenta-1,4-diyne in low yield. Hydrogenation with Pd/H_2 then afforded the desired product (**5**). Comparison

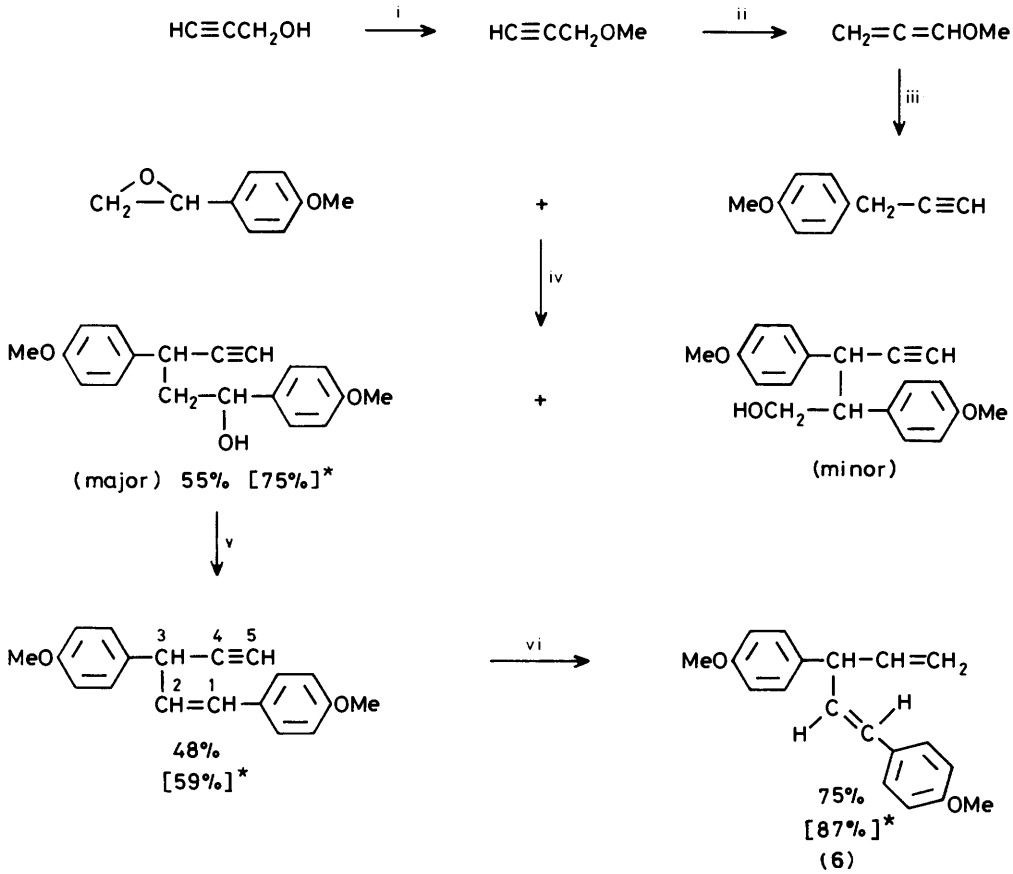


Scheme 1. Synthesis of (*Z*)-3-(4-methoxyphenyl)-1-phenylpenta-1,4-diene (**5**). *Reagents:* (i), Ac_2O–$MeCO_2H$; (ii), PhC≡CMgBr; (iii), Pd on $CaCO_3$, H_2

of the spectral data of (**5**) for protons on C(1), C(2), and C(3) with those obtained for the corresponding protons for the hinokiresinol[11] derivative and the nyasol derivative[7] (Table 1) leaves little doubt that these three compounds all possess a 1,2-*Z* configuration.

Synthesis of 1,2-E *Compounds* (**6**) *and* (**7**).—For our second route, which forms the major part of this work, we have utilized the regiospecific functionalization of the propargylic site of dilithio salts of alk-1-ynes as described by Brandsma and coworkers.[12] In contrast to our first route above, the propargylic carbon now acts as a powerful *nucleophile* and will react with suitable electrophiles. Benzylacetylene was prepared in good yield from readily available prop-2-yn-1-ol by standard procedures.[13] Reaction of its dilithium salt with styrene oxide and with 4-methoxystyrene oxide afforded the desired alcohol in good yield (Scheme 2). It was not possible to suppress entirely formation of the 'wrong' alcohol at this stage, but a good separation was effected by column chromatography. Dehydration of the alcohol under mild acidic conditions readily gave the pent-4-en-1-yne derivative and this was finally reduced with Lindlar's catalyst to the desired penta-1,4-diene derivative.

As outlined earlier, compound (**5**), obtained from the 'acetate route' (Scheme 1), had identical stereochemistry to the nyasol derivative described by Marini-Bettolo.[7] By contrast, compounds (**6**) and (**7**) obtained by the 'propargyl route' (Scheme 2) possessed a different stereochemistry. The only difference possible between these compounds involves the stereochemistry round the C(1)–C(2) double bond and our spectral data (below)



Scheme 2. Synthesis of (*E*)-1,3-bis-(4′-dimethoxyphenyl)penta-1,4-diene (**6**). *Reagents and conditions:* (i), Me_2SO_4–KOH; (ii), K^+ $^-OBu^t$; (iii), $MeOC_6H_4MgBr$–CuI; (iv), 2 × BuLi, −20 °C; (v), H^+, SiO_2; (vi), Pd on $CaCO_3$, H_2

* Figures in square brackets represent the yields of products obtained in the synthesis of compound (**7**).

Table 1. Chemical shifts (δ_H) and coupling constants for protons on C-1, C-2, and C-3 for compounds (**4**) and (**5**)

	(**4**) Whiting [11]	(**4**) Marini-Bettolo [7]	(**5**)[a]
1-H	6.60, *J* 12 Hz	6.66, *J* 11 Hz	6.56, *J* 11.3 Hz
2-H	5.80, *J* 12 Hz	5.80, *J* 11 Hz	5.77, *J* 11.3 Hz
3-H	4.60	4.64	4.56

[a] This work.

suggest that the natural product has a *Z*-configuration whereas our two products (Scheme 2) possess an *E*-configuration.

^{1}H *N.m.r. and* ^{13}C *N.m.r. Investigation of the Synthetic Products* (**6**) *and* (**7**).—In their characterization of the dimethyl ether of hinokiresinol, Whiting and Beracierta [11] quote limited spectroscopic data and several of the peak groups in the proton spectrum are labelled as multiplets. From the relatively large $J_{1,2}$ value (12 MHz) these authors conclude that dimethylhinokiresinol has *E*-stereochemistry. However, they do point out that this coupling constant for compound (**4**) is markedly lower than $J_{1,2}$ for the closely related agatharesinol (**9**) ($J_{1,2}$ 16 Hz), 'but the origins of this difference are not apparent to us'. Marini-Bettolo *et al.*[7] report a detailed proton analysis (at 100 MHz) of nyasol dimethyl ether (**4**) but refrain from comment on its stereochemistry. The peak due to the proton attached to C(4) is described as a multiplet and the resolution of some of the other peaks is poor.

Scrutiny of available organic literature for penta-1,4-dienes [14,15] has shown that the ABX system due to protons on C(2), C(1), and C(3) and that due to protons on C(3), C(4), and C(5) is recorded for a large number of naturally occurring compounds but only very rarely has a detailed analysis been undertaken. Our own results, recorded at 500 MHz for compound (**7**), allow for an unambiguous assignment of all the protons present with accurate measurement of all the relevant coupling constants. On the basis of these values our synthetic products (Scheme 2) possess *E*-stereochemistry with $J_{1,2}$ 15.9 Hz.

Compounds (**6**) and (**7**) differ by only one methoxy group on the benzene ring. From a comparison of their proton and carbon spectra at 80 and 20 MHz respectively it was clear that they had identical stereochemistry. Since compound (**7**) was the more stable, and more of it was available, it was examined at high field. The two protons on C(5), H_P and H_Q give rise to four sets of doublets of doublets on account of long-range coupling with the proton on C(3). This latter proton is not clearly resolved and is best described as two sets of doublets of doublets. The proton on C(4) gives rise to seven signals which represent a partial overlap of two sets of doublets of doublets.

The two protons on C(1) and C(2), which are coupled to the proton on C(3), give rise to six signals, of which one is very prominent. They present an excellent example of what has been termed a 'deceptively simple' ABX spectrum.[16] Partial overlap of some peaks and also the extremely small size of others transforms two classical sets of doublets of doublets into the observed pattern. Since the six protons present in the alkene chain of compound (**7**) give rise to a spectrum which cannot be interpreted by first-order analysis, spectral parameters were determined by the method described by Corio [17] and these are shown below.

Determination of the Spectral Parameters of the Non-ring Protons of Compound (**7**).—Assignment of the 3-H proton at δ_H 4.10 was fairly obvious. Published information [7,11,14] aided the allocation of the two protons on C(5) at δ_H 4.95—5.20. Protons 1-H and 2-H lie furthest downfield as expected, between δ_H 6.30 and 6.45. The highly complex signal located at δ_H 5.80—6.30 (integrating for 1 proton) was assigned to 4-H and this was confirmed by comparison with published spectra.[7,11]

The protons of interest thus fall into two distinct systems: an ABX system for protons 2, 1, and 3 respectively and a KPQX system for protons 4, 5, and 3 respectively.

Table 2. Chemical shifts (δ_H) and coupling constants (Hz) for compound (**7**)

Proton designation	Chemical shift	Coupling constant
A	6.40	J_{KP} 10.15
B	6.42	J_{KQ} 17.15
K	6.10	J_{KX} 6.75
P	5.18	J_{PQ} 1.55
Q	5.13	J_{PX} 1.11
X	4.18	J_{QX} 1.27
		J_{AB} 15.90
		J_{AX} 7.01
		J_{BX} 1.64

The ABX System.—Using parameters extracted from the 500 MHz ^{1}H spectrum and employing resolution-analysis techniques [17] for the two pseudo-AB quartets, the following values were calculated:

J_{AB} 15.9 Hz; $(J_{AX} + J_{BX})$ 5.37 Hz
D_+ 11.70 Hz; D_- 9.02 Hz.

This allowed determination of two possible sets of parameters:

$(J_{AX} - J_{BX})$ $\pm$8.662 Hz or $\pm$25.837 Hz
J_{AX} $\pm$7.016 Hz or $\pm$15.522 Hz
J_{BX} $\mp$1.646 Hz or $\mp$10.152 Hz
$\gamma_0\Delta_{AB}$ $\pm$12.818 Hz or $\pm$4.336 Hz

It was hoped that determination of the correct set of parameters would be facilitated by comparison of simulated spectra of the 'X' region, using permutations of these parameters. This indeed proved to be the case, and resulted in the selection of the following values:

J_{AX} 7.01 Hz; J_{BX} $\mp$1.64 Hz

The assignment was subsequently checked by simulation of the full ABKPQX spectrum with both sets of parameters and was found to be unambiguous.

The values of δ_A and δ_B were determined by simulation of the AB region and subsequent measurement of absorption bands and comparison with the 500 MHz spectrum. This enabled the following values to be determined.

δ_A 6.40 p.p.m.; δ_B 6.42 p.p.m.

The KPQX System.—The determination of the KPQX system was initiated by a visual comparison of the individual resonances of each proton. From this, approximate coupling constants and shifts were extracted and a simulation undertaken. By varying these parameters in order to obtain reasonable matches the values shown in Table 2 were obtained.

The results of the full ABK PQX system simulations and the experimental data were compared and found to be good matches (Figures 1 and 2).

Experimental

M.p.s were determined on a Kofler block and are uncorrected. ^{1}H N.m.r. and ^{13}C n.m.r. spectra were recorded either on a

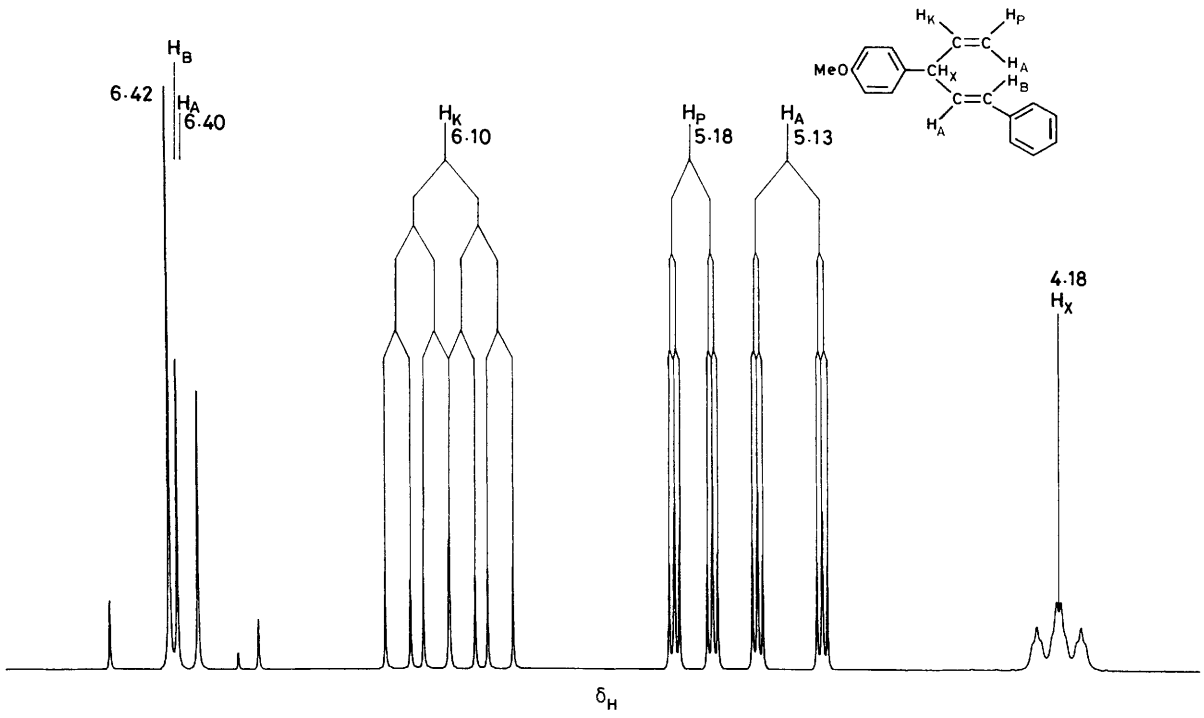


Figure 1. Simulated ^{1}H n.m.r. spectrum of compound (7)

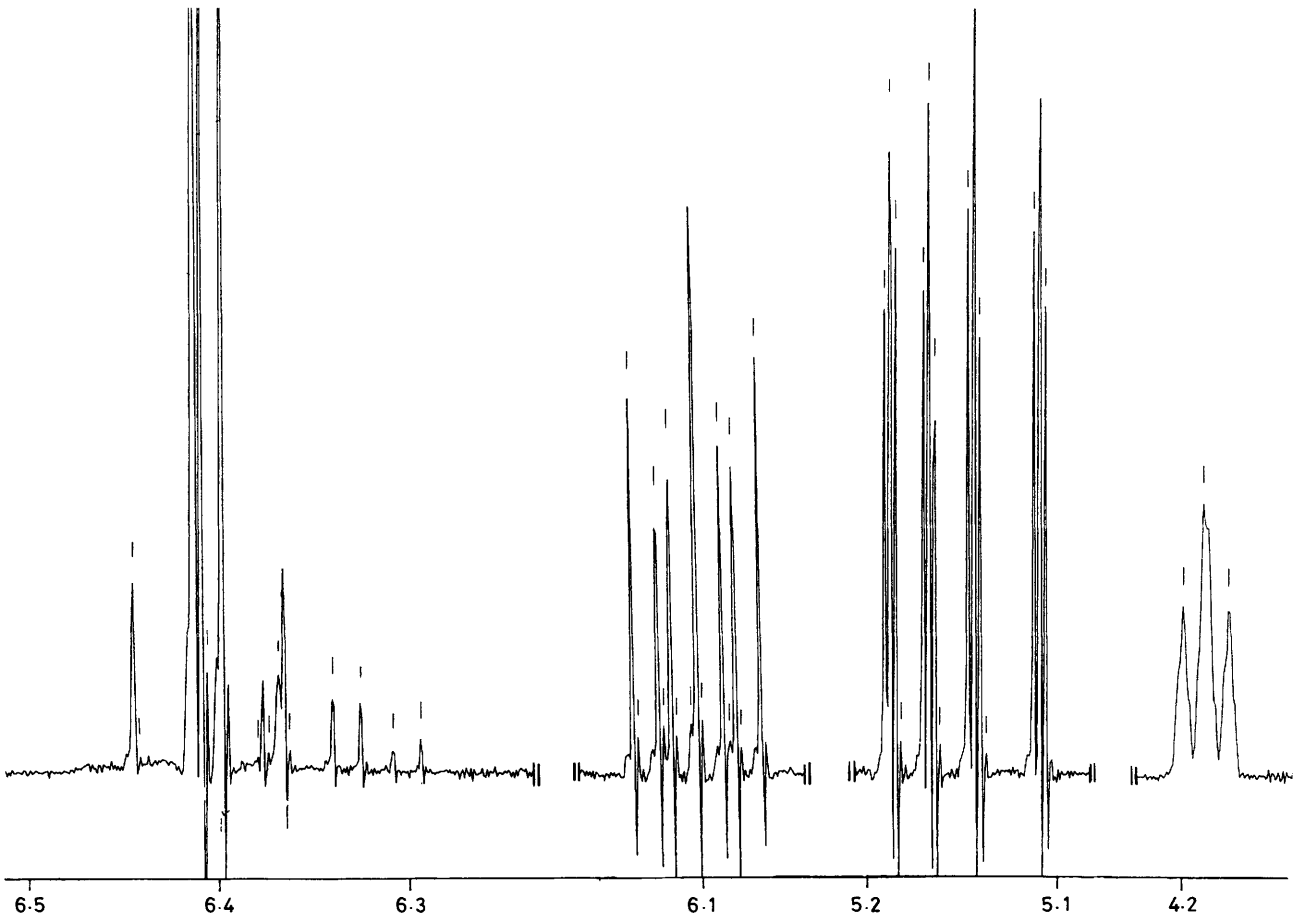


Figure 2. Experimental 500 MHz ^{1}H n.m.r. spectrum of compound (7)

Varian FT 80A or a Brüker WM500 (500 MHz) spectrometer. For mass spectra a Varian MAT 212 and a Hewlett Packard 5998A were employed. Light petroleum refers to the fraction boiling in the range (40—60 °C).

1-(4-*Methoxyphenyl*)*prop*-2-*yn*-1-*ol*.—This was prepared in 95% yield from *p*-anisaldehyde and acetylene using essentially the procedure of Whalley and co-workers.[18] Instead of sodium acetylide, the alkynide anion was generated from ethylmagnesium bromide. The product distilled at 106 °C at 2 mmHg and subsequently crystallized, m.p. 34 °C. ^{1}H and ^{13}C N.m.r. and mass spectra confirmed the purity of the compound.

3-*Acetoxy*-3-(4-*methoxyphenyl*)*prop*-1-*yne*.—Toluene-4-sulphonic acid (200 mg), acetic anhydride (15 ml), and glacial acetic acid (4 ml) were cooled to 0 °C. A solution of the above alkynol (0.5 g, 3.1 mmol) in acetic anhydride (4 ml) was added rapidly and the reaction was allowed to proceed for 30 min. From the very dark solution, the desired product was obtained by distillation (76%) whereupon it crystallized, m.p. 36 °C. The large excess of acetic anhydride is necessary to prevent dimerization to the ether.

3-(4′-*Methoxyphenyl*)-1-*phenylpenta*-1,4-*diyne*.—Phenylacetylene (0.339 g, 3.33 mmol) was added to ethylmagnesium bromide [3.33 mmol, generated in tetrahydrofuran (THF) from ethyl bromide (0.362 g) and Mg metal (0.08 g)]. After 30 min at 25 °C, this suspension was added to the above acetate (0.8 g, 3.06 mmol) at −10 °C and was stirred at this temperature for 1h. The reaction mixture was quenched with saturated aq. ammonium chloride, concentrated under reduced pressure, and extracted with ether. Column chromatography [SiO_2; light petroleum–ethyl acetate (4:1) as eluant] afforded starting material (480 mg) and the required dialkyne (130 mg, 31%), δ_H($CDCl_3$; 80 MHz) 2.38 (1 H, d, *J* 2.62 Hz, C≡CH), 3.77 (3 H, s, OMe), 4.91 (1 H, d, *J* 2.60 Hz, C*H*C≡CH), 6.90 (2 H, d, *J* 8.87 Hz, 2′ and 6′-H), 7.50 (2 H, d, *J* 8.87 Hz), 3′- and 5′-H), and 7.20—7.56 (5 H, m, Ph); δ_C 28.27 (H*C*C≡CH), 55.41 (OMe), 70.90 (C≡*C*H), 81.74 (*C*≡CAr), 82.90 (HC*C*≡CH), 86.53 (C≡*C*Ar), 114.28 (d), 122.97 (s), 128.34 (d), 128.39 (d), 129.56 (s), 131.89 (d), and 159.25 (s).

(Z)-3-(4-*Methoxyphenyl*)-1-*phenylpenta*-1,4-*diene* (**5**).—The dialkyne (50 mg, 0.203 mmol) in methanol (30 ml) was hydrogenated over Lindlar's catalyst (10% Pd–$CaCO_3$. Reaction was monitored on t.l.c. [light petroleum–ethyl acetate (6:1)]. In order to prevent over-hydrogenation, the reaction was stopped when about half the starting material had reacted. Separation on a column [SiO_2; light petroleum–ether (295:5)] gave the *title diene* as a pale yellow oil (20 mg) (Found: M^+, 250.1353. $C_{18}H_{18}O$ requires *M*, 250.1358); δ_H($CDCl_3$; 80 MHz) 3.77 (3 H, s, OMe), 4.56 (1 H, br dd, 3-H), 5.13 (1 H, m, 5-H), 5.17 (1 H, m, 5-H), 6.04 (1 H, br m, 4-H), 5.77 (1 H, dd, *J* 10.02, 11.3 Hz, 2-H), 6.56 (1 H, d, *J* 11.3 Hz, 1-H), and 6.8—7.3 (9 H, m, ArH); *m*/*z* 250 (M^+, 85%), 235 (50), 223 (M^+ − CH=CH_2, 29; Found: 223.1122. $C_{16}H_{15}O$ requires *m*/*z* 223.1123), 159 (50), 121 (100), 115 (85), 103 (30), and 91 (100).

3-(4-*Methoxyphenyl*)*prop*-1-*yne*.—Using the methods of Brandsma[12] and of Vermeer,[13] prop-2-yn-1-ol was converted into methoxyallene, which reacted with 4-methoxybromobenzene in the presence of copper(I) chloride to afford the title compound in high yield, b.p. 95 °C at 12 mmHg; δ_H($CDCl_3$; 60 MHz) 2.17 (1 H, t, C≡CH), 3.57 (2 H, d, *J* 3.8 Hz, CH_2), 3.80 (3 H, s, OMe), 6.90 (2 H, d, *J* 9.2 Hz, ArH), and 7.33 (2 H, d, *J* 9.2 Hz, ArH).

3-(4-*Methoxyphenyl*)-1-*phenylpent*-4-*yn*-1-*ol*.—A solution of 3-(4-Methoxyphenyl)prop-1-yne (1.46 g, 0.01 mol) in dry THF was cooled to −30 °C. Butyl-lithium (16.6 ml, 0.02 mol; 1.5M in hexane) was then added and the temperature was maintained at −20 °C. The solution became dark brown and was then allowed to warm to 27 °C at which temperature it was stirred for a further 4 h.[19] It was then cooled to −20 °C and a solution of styrene oxide (1.2 g, 0.01 mol) in THF (10 ml) was added dropwise during 10 min. The mixture was allowed to warm to 10 °C, was stirred for 1.5 h at this temperature, and was then quenched with ice–water at 7 °C. Extraction with ether and concentration under reduced pressure gave oil (2.2 g), which was purified by flash chromatography [SiO_2; light petroleum–ethyl acetate (5:1)]. This afforded the title compound (1.4 g, 75%) and 2-*phenyl*-3-(4′-*methoxyphenyl*)*pent*-4-*yn*-1-*ol* (0.46 g, 25%) (Found for the major isomer: C, 82.5; H, 7.2. $C_{18}H_{18}O_2$ requires C, 82.0; H, 7.0%); δ_H($CDCl_3$; 80 MHz) 1.99 (2 H, t, CH_2), 2.30 (1 H, d, *J* 2.55 Hz, C≡CH, 3.04 (1 H, br s, OH), 3.63 (3 H, s, OMe), 3.93 (1 H, m, 3-H), 4.93 (1 H, br t, 2-H), 6.73 (2 H, d, *J* 8.7 Hz, ArH), and 7.13—7.31 (7 H, m, ArH); δ_C($CDCl_3$) 33.49 (d, C-3), 47.11 (t, C-1), 55.17 (q, OMe), 71.95 (d, C≡*C*H), 72.08 (d, C-2), 85.89 (s, *C*≡CH, and 114.03, 125.76, 127.46, 128.44, 128.49, 133.36, 144.48, and 158.73 (s, C-4′).

1,3-*Bis*-(4′-*methoxyphenyl*)*pent*-4-*yn*-1-*ol*.—This compound was obtained from 3-(4-methoxyphenyl)prop-1-yne and 4-methoxystyrene oxide[19] in 55% yield by the procedure described above. The *light yellow oil* was likewise purified by chromatography (Found: C, 76.6; H, 7.2. $C_{19}H_{20}O_3$ requires C, 76.9; H, 6.8%); δ_H($CDCl_3$; 80 MHz) 2.03 (2 H, t, CH_2), 2.30 (1 H, d, *J* 2.55 Hz, C≡CH), 3.0 (1 H, br s, OH), 3.67 (6 H, s, OMe), 3.90 (1 H, m, 3-H), 4.89 (1 H, t, 1-H), 6.78 (4-H, d, *J* 8.62 Hz, ArH), 7.21 (2 H, d, *J* 8.62 Hz, ArH), and 7.24 (2 H, d, *J* 8.62 Hz, ArH); δ_C($CDCl_3$; 20 MHz) 33.67 (d, C-3), 47.62 (t, CH_2), 55.10 (q, 2 × OMe), 71.42 (d, C≡*C*H), 71.60 (d, C-1), 85.95 (s, *C*≡CH), 113.79 (d, Ar-C), 113.96 (d, Ar-C), 127.00 (d, Ar-C), 128.28 (d, Ar-C), 133.64 (s, Ar-C), 136.64 (s, Ar-C), 158.34 (s, C-4′), and 158.85 (s, C-4″).

3-(4-*Methoxyphenyl*)-1-*phenylpent*-1-*en*-4-*yne*.—Acidified silica gel was prepared by the method of Scettri.[20] The above acetylenic alcohol (500 mg) was heated in benzene (25 ml) for 3 h at 40 °C with the dehydrating reagent (8 g). Progress of the reaction was readily followed by t.l.c. using light petroleum–ethyl acetate (5:1). The dark brown silica gel was separated from the mixture by filtration through a short (2.5 cm) silica gel column with benzene as eluant. From the filtrate a yellow oil was obtained (275 mg, 59%) which was purified by flash chromatography (SiO_2) to afford the pure pentenyne (230 mg) (Found: M^+, 248.1201. $C_{18}H_{16}O$ requires *M*, 248.1202); δ_H($CDCl_2$; 80 MHz) 2.46 (1 H, d, *J* 2.54 Hz, C≡CH), 3.77 (3 H, s, OMe), 4.45 (1 H, ddd, *J* 0.99, 2.55, and 6.17 Hz, 3-H), 6.18 (1 H, dd, *J* 6.08, 15.70 Hz, 2-H), 6.68 (1 H, dd, *J* 1.35, 15.63 Hz, 1-H), 6.82 (2 H, d, *J* 8.82 Hz, ArH), and 7.0—7.4 (7 H, m, ArH); *m*/*z* 248 (M^+, 100%), 233 (26), 217 (45), 215 (46), 202 (51), 170 (83), 145 (32), 139 (74), 115 (61), 102 (54), and 91 (28).

1,3-*Bis*-(4′-*methoxyphenyl*)*pent*-1-*en*-4-*yne*.—1,3-Bis-(4′-methoxyphenyl)pent-4-yn-1-ol was dehydrated by the procedure described above. In this case no heat was necessary and the reaction was essentially complete in 4 h. Work-up afforded the *title compound* as a yellow oil in 48% yield (Found: M^+, 278, 132 71. $C_{19}H_{18}O_2$ requires *M*, 278.130 68); δ_H($CDCl_3$; 80 MHz) 2.39 (1 H, d, *J* 2.53 Hz, C≡CH), 3.72 (6 H, s, OMe), 4.37 (1 H, br d, *J* 6.0 Hz, 3-H), 5.98 (1 H, dd, *J* 6.17, 15.62 Hz, 2-H), 6.56 (1 H, d, *J* 15.3 Hz, 1-H), 6.71 (2 H, d, *J* 8.81 Hz, ArH), 6.75 (2 H, d, *J* 8.81 Hz, ArH), 7.21 (2 H, d, *J* 8.80 Hz, ArH), and 7.23 (2 H, d, *J* 8.79 Hz, ArH); δ_C ($CDCl_3$; 20 MHz) 39.72 (d, C-3), 55.02

(q, 2 × OMe), 73.33 (d, C≡CH), 84.13 (s, C≡CH), 114.07, 114.16 (d, C-3′, -5′ and -3″, -5″), 127.41 (s, C-1′), 127.78 and 128.78 (d, C-2′, 6′ and -2″, -6″), 132.14 (s, C-1″), 129.69 and 129.94 (d, C-1 and -2), 158.92 (s, C-4′), and 159.42 (s, C-4″); *m/z* 278 (M^+, 100%), 263 (28), 247 (54), 232 (22), 220 (11), 215 (23), 203 (23), 202 (25), 189 (22), 170 (91), 155 (31), 145 (27), 139 (34), 133 (32), 121 (42), and 115 (29).

3-(4-*Methoxyphenyl*)-1-*phenylpenta*-1,4-*diene* (**7**).—The alkyne (195 mg) was dissolved in methanol (20 ml) and hydrogenated at atmospheric pressure at 25 °C using 10% Pd/C as catalyst. After 2 h, reaction was complete as judged by the appearance of a new spot of higher R_F on t.l.c. plates [light petroleum–ethyl acetate (5:1)]. Evaporation of the solvent gave the *title diene* as a pale yellow oil (170 mg, 87%) (Found: M^+, 250.1358. $C_{18}H_{18}O$ requires *M*, 250.135 77); $\delta_H(CDCl_3)$; 500 MHz) *inter alia* 3.70 (3 H, s, OMe), 4.18 (1 H, br t, *J* 6.6 Hz, 3-H), 6.82 (2 H, d, *J* 8.75 Hz, ArH), and 7.03—7.38 (7 H, m, ArH). Spectral data for the five non-ring protons are shown in Table 1 and Figure 2; $\delta_C(CDCl_3$; 125 MHz) 51.51 (d, C-3), 55.26 (q, OMe), 113.96 (d, C-3″, -5″), 115.31 (t, C-5), 126.08 (d, C-2″, -6″), 127.15 (d, C-4′), 128.54 (d, C-2′, -6′), 129.00 (d, C-3′, -5′), 130.37 (d, C-2), 132.06 (d, C-1), 134.62 (s, C-1′), 137.41 (s, C-1″), 140.28 (d, C-4), and 158.26 (s, C-4″); *m/z* 250 (M^+, 66%), 235 (16), 223 (47), 219 (10), 203 (7), 202 (6), 189 (6), 179 (8), 172 (13), 165 (16), 159 (31), 152 (9), 145 (25), 142 (28), 141 (26), 129 (27), 121 (58), 115 (100), 102 (16), and 91 (87).

1,3-*Bis*-(4′-*methoxyphenyl*)*penta*-1,4-*diene* (**6**).—The above bis(methoxyphenyl)alkyne (180 mg) was hydrogenated as above at 25 °C for 90 min. This afforded the *title diene* as a pale yellow oil (135 mg, 75%) (Found: M^+, 280.148 45. $C_{19}H_{20}O_2$ requires *M*, 280.146 33); $\delta_H(CDCl_3$; 80 MHz) 3.75 (6 H, s, OMe), 4.13 (1 H, t, *J* 6.6 Hz, 3-H), 5.07 (1 H, ddd, J_{PQ} 1.67, J_{QX} 1.60, J_{QX} 17.67 Hz, 5-H_Q), 5.13 (1 H, ddd, J_{PQ} 1.67 J_{PX} 1.60, J_{PK} 9.93 Hz, 5-H_P), 6.04 (1 H, ddd, 4-H), 6.26 (1 H, dd, *J* 15.9 Hz, 2-H), 6.29 (1 H, dd, *J* 15.9 Hz, 1-H), 6.80 (2 H, d, *J* 8.71 Hz, 3″-, 5″-H), 6.83 (2 H, d, *J* 8.75 Hz, 3′-, 5′-H), 7.17 (2 H, d, *J* 8.75 Hz, 2″-, 6″-H), and 7.28 (2 H, d, *J* 8.75 Hz, 2′-, 6′-H); $\delta_C(CDCl_3$; 20 MHz) 51.66 (d, C-3), 55.37 (q, OMe), 114.09 (d, C-3″, -5″ and -3′, -5′), 115.30 (t, C-5), 127.49 (d, C-2″, -6″), 129.16 (d, C-2′, -6′), 129.93 (s, C-1′), 130.08 (d, C-2), 130.41 (d, C-1), 135.04 (s, C-1″), 140.73 (d, C-4), 158.40 (s, C-4′), and 159.11 (s, C-4″); *m/z* 280 (M^+, 100), 265 (29), 253 (66), 172 (54), 159 (44), 145 (99), 133 (28), 121 (96), 115 (38), and 91 (29).

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