Asymmetric Syntheses. Part VIII.[1] † Asymmetric Synthesis of β-Allenic Alcohols with the Lithium Aluminium Hydride–3-*O*-Benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose Complex; Determination of the Absolute Configuration of Marasin (Nona-3,4-diene-6,8-diyn-1-ol) and 9-Methylmarasin (Deca-3,4-diene-6,8-diyn-1-ol)

By **Stephen R. Landor,*‡ Brian J. Miller, John P. Regan,** and **Austin R. Tatchell,** Fourah Bay College, University of Sierra Leone; Woolwich Polytechnic, London SE18; and Makerere University, Kampala, Uganda

The following asymmetric reductions with the lithium aluminium hydride–3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose complex were carried out. Hex-2-en-4-yn-1-ol gave (−)-hexa-3,4-dienol, $[\alpha]_D^{20}$ −10°; hept-2-en-4-yn-1-ol gave (−)-hepta-3,4-dienol, $[\alpha]_D^{20}$ −8·9°; non-2-en-4-yn-1-ol gave nona-3,4-dienol, $[\alpha]_D^{20}$ −7·4°; 5-phenylpent-2-en-4-yn-1-ol gave 5-phenylpenta-2,3-dienol, $[\alpha]_D^{20}$ −16·4°; 8,8-dimethylnon-2-en-4,6-diyn-1-ol gave (−)-8,8-dimethylnona-3,4-dien-6-yn-1-ol, $[\alpha]_D^{25}$ −12·5°; 7-phenylhept-2-en-4,6-diyn-1-ol gave 7-phenylhepta-3,4-dien-6-yn-1-ol, $[\alpha]_D^{25}$ −3·1°; non-2-ene-4,6,8-triynyl-1-ol gave (−)-marasin, $[\alpha]_D^{25}$ −26·6°; and dec-2-ene-4,6,8-triyn-1-ol gave 9-methylmarasin, $[\alpha]_D^{25}$ −11·3°. The absolute configuration of all the β-allenic alcohols thus obtained is deduced as *R*.

In the preceding paper[1] it was shown that partially resolved (+)-hexa-3,4-dien-1-ol and (+)-hepta-3,4-dien-1-ol may be obtained by asymmetric reduction of the corresponding enynols with lithium bismenthyloxyaluminium hydride, and that the absolute configuration of the products is *S*. Application to the synthesis and determination of the absolute configuration of (+)-marasin was foiled by difficulties in the separation of traces of the C_{10} (−)-menthol from the C_9 (+)-marasin in the product.

The asymmetric reduction of enynols with the lithium aluminium hydride–3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose complex [2a] by-passed this problem, as allenic alcohols are readily separated from the monosaccharide derivative resulting from the hydrolysis of the complex either by distillation (if the allenic alcohol is stable) or by chromatography of the more sensitive diynallenols.[2b]

$$RC{\equiv}C{\cdot}CH{=}CH{\cdot}CH_2{\cdot}OH + \overset{+}{L}i\bar{A}lH_2C_{19}H_{24}O_6 \longrightarrow RCH{=}C{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$$

The asymmetric reduction of alkenynols with lithium bismenthyloxyaluminium hydride was shown to be thermodynamically controlled,[1] and inspection of models of the two enantiomeric forms of the seven-membered cyclic allene complex predicted that the more stable *S*-isomer should be formed in excess. As the chiral allenols thus obtained had (+)-rotations they were assigned the (+)-*S* configuration and this was independently confirmed. By the same argument the asymmetric reduction with the lithium aluminium hydride–3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose complex must also be thermodynamically controlled but the more stable complex now has the *R*-configuration. Evidence for this was obtained by reduction of hex-1-en-4-yn-1-ol with lithium aluminium hydride to the aluminohydride–allene complex, followed by addition of the chiral monosaccharide reagent, which gave (−)-hexa-3,4-dienol (R = Me), $[\alpha]_D^{20}$ −8·2 (*cf.* $[\alpha]_D^{20}$ −10° for the same chiral allenol obtained by reduction with preformed monosaccharide complex). Therefore the same *R*- and *S*-allene complexes are formed by either method, with the (−)-*R*-form predominating in each case. The seven-membered cyclic allene complex (see Scheme) is again the most convenient representation; the *R*-form (II) is thermodynamically the more stable, as it has the least non-bonded interactions. Both *R*- and *S*-tetrahedral complexes (II) and (III) are formed reversibly from the initial planar, trigonal aluminium allenide anion (I) so that, at equilibrium, the more stable *R*-form will predominate. The (−)-*R*-isomer is therefore always formed predominantly. Inspection of models of the *R*- and *S*-forms of the alternative, strainless fourteen-membered cyclic complex (IV) predicts the same stereochemical result.

Ten examples of the reduction of alkenynols have so far been studied; in each case the resulting β-allenic alcohol had a negative rotation (see Table 1). A wide variety of alkyl, alkenyl, and alkynyl substituents on the acetylenic C-5 have given consistent results and it may be concluded that all laevorotatory β-allenic alcohols of this type have the *R*-configuration and all dextrorotatory compounds the *S*-configuration. The maximum rotation reported for the four naturally occurring allenes, marasin (R = H[C≡C]$_2$), 9-methylmarasin (R = Me[C≡C]$_2$), and laballenic (R = Me[CH$_2$]$_{10}$) and lamenallenic (R = MeCH=CH[CH$_2$]$_8$) acids permits the stereoselectivity of the asymmetric reduction to be calculated (see Table 1; the maximum stereoselectivity obtained so far is 11·6% for hexadexa-3,4-*trans*-14-trien-1-ol). An application of Brewster's theory [3] also predicts the *R*-configuration for laevorotatory β-allenic alcohols.

† This paper is also considered as Part XXX in the series entitled Allenes; Part XXIX, preceding paper.

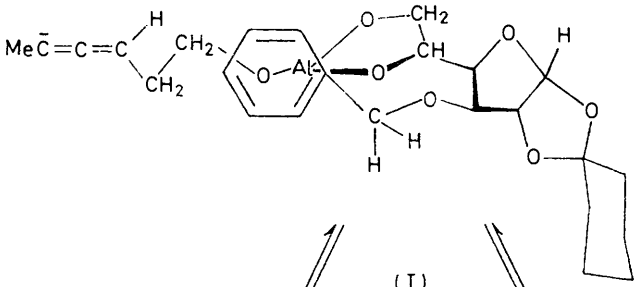
‡ *Present address:* Department of Chemistry, Exeter University, Exeter EX4 4QD.

[1] Part VII, R. J. D. Evans, S. R. Landor, and J. P. Regan preceding paper.

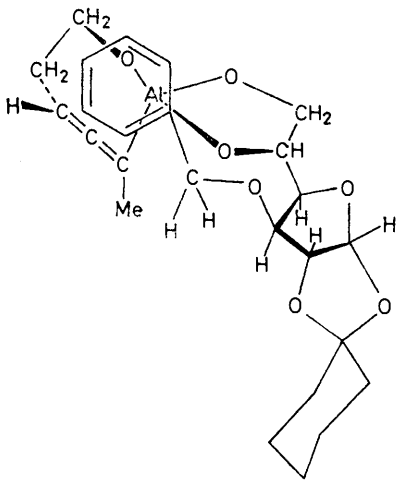
[2] (*a*) S. R. Landor, B. J. Miller, and A. R. Tatchell, *J. Chem. Soc.* (*C*), 1966, 1822; (*b*) preliminary communication, S. R. Landor, B. J. Miller, J. P. Regan, and A. R. Tatchell, *Chem. Comm.*, 1966, 585.

[3] J. H. Brewster, *J. Amer. Chem. Soc.*, 1959, **81**, 5475; G. Lowe, *Chem. Comm.*, 1964, 411; J. H. Brewster, *Topics Stereochem.*, 1967, 133.

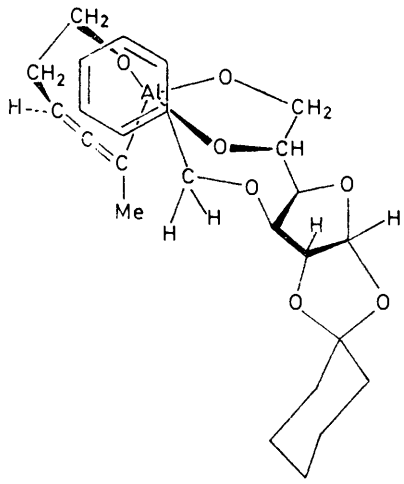
Special precautions had to be taken with the two naturally occurring diynallenols,[4] marasin (R = H[C≡C]$_2$) and 9-methylmarasin (R = Me[C≡C]$_2$). It was essential to use analytically pure 3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose [2] for complexing with lithium aluminium hydride, otherwise traces of a dibenzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose are eluted in the same fractions as marasin and 9-methylmarasin during chromatography. Dilute solutions (<0·5%) of optically active marasin and 9-methylmarasin are reasonably stable and retain their optical activity at 0° in the dark; more concentrated solutions (>2%) rapidly lose optical activity, and only part of the marasin can be recovered. Complete racemisation also ensued when a 0·01% solution of (−)-marasin in aqueous methanolic 5% hydrochloric acid was kept at room temperature for 2 h, although pure, racemic marasin could be recovered quantitatively by dilution with water and extraction with ether.



(I)

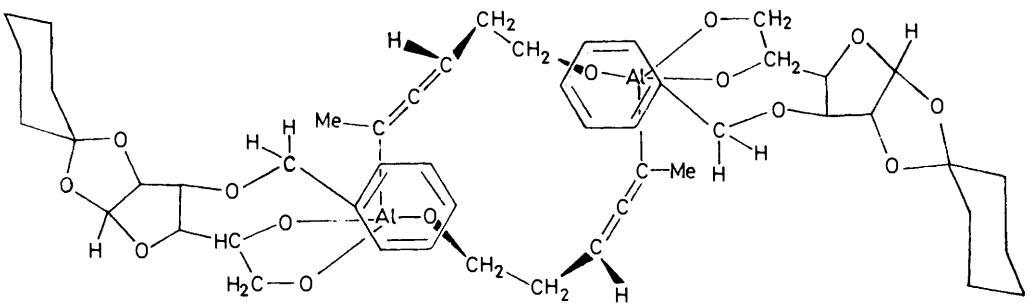


(*R*)-(II)



(*S*)-(III)

SCHEME

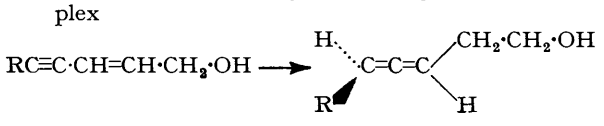


Tables 2—5 show that maximum stereoselectivity is obtained by using a ratio of lithium aluminium hydride to monosaccharide of 1 : 0·73 and a four-fold excess of reducing complex.

[4] G. Bendz, *Arkiv Kemi*, 1959, 305; R. E. Bew, J. R. Chapman, E. R. H. Jones, B. E. Lowe, and G. Lowe, *J. Chem. Soc.* (*C*), 1966, 129.

TABLE 1

Asymmetric reduction of alkenynols to (−)-(*R*)-allenic alcohols with the lithium aluminium hydride–3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose complex



R	Configuration	$[\alpha]_D^{25}$(°)	% e.e.†
Me	*R*	−10	
Et	*R*	−8·9	
Bu^n	*R*	−7·4	
Ph	*R*	−12·5	
$Bu^tC{\equiv}C$	*R*	−12·5	
Ph—C≡CH	*R*	−3·1	*
$H[C{\equiv}C]_2$	*R*	−26·6	
$Me[C{\equiv}C]_2$	*R*	−11·3	3·3*
$Me[CH_2]_{16}$ ‡	*R*	−3·0	6·3*
$Me{-}CH{=}CH{\cdot}[CH_2]_8$ ‡	*R*	−5·8	11·6

* The 1 : 1 ratio of $LiAlH_4$ to monosaccharide used here for (−)-9-methylmarasin, (−)-7-phenylhepta-3,4-dien-6-yn-1-ol, and (−)-laballenic acid has been shown (see Tables 2—5) to give only half the optimum stereoselectivity. These experiments were performed before the optimum conditions had been established. † e.c. = excess of enantiomer. ‡ J. S. Cowie, P. D. Landor, S. R. Landor, and N. Punja, *J.C.S. Perkin I*, 1972, 2197.

EXPERIMENTAL

For general remarks, see preceding paper. T.l.c. was carried out on 20 cm^2 plates of silica gel (Merck Kieselgel G) (250 μm thick) with 2% methanol in benzene as solvent system; the spray reagent was an ethanolic 0·2% solution of naphthoresorcinol to which 10% of phosphoric acid had been added. Rotations were determined with a Stanley polarimeter and a Bendix photoelectric polarimeter.

(−)-*Hexa*-3,4-*dien*-1-*ol*.—(*a*) A solution of 3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose [2] (47 g, 0·134 mol) in dry ether (120 ml) was added dropwise over 45 min to a stirred suspension of lithium aluminium hydride (7·0 g, 0·184 mol) in dry ether (240 ml). The mixture was heated under reflux for 90 min; then hex-2-en-4-yn-1-ol (3·2 g, 0·033 mol) in dry ether (50 ml) was added over 30 min. Heating was continued for 4 h; the mixture was then cooled, the complex was decomposed by addition of water (50 ml), the precipitated hydroxides were removed by filtration through kieselguhr, and the ethereal solution was dried and evaporated. The products were separated from the monosaccharide derivative by distillation under reduced pressure and gave as the main fraction hexa-3,4-dien-1-ol (1·5 g, 46%), b.p. 46—48° at 2 mmHg, $[\alpha]_D^{20}$ −10·0°, $\nu_{max.}$ 3400—3300 (OH), 1960 (C=C=C), and 1050—1040 cm^{-1} (C–O), g.l.c. t_R 4·5 min (silicone oil; 148°). Three further

TABLE 2

Reduction of hex-2-en-4-yn-1-ol

$LiAlH_4$		Glucofuranose derivative		Hex-3-en-4-yn-1-ol		Hexa-3,4-dien-1-ol			
						Yield		B.p.(°C) [mmHg]	$[\alpha]_D^{20}$(°)
g	mol	g	mol	g	mol	g	%		
3·5	0·092	23·3	0·057	3·2	0·033	1·5	46	70—72 [5]	−4·0
4·0	0·105	23·3	0·057	3·2	0·033	1·5	46	42 [1·6]	−6·5
5·5	0·145	47·0	0·134	3·2	0·033	1·2	37	56—60 [4]	−5·3
7·0	0·184	47·0	0·134	3·2	0·033	1·5	46	46—48 [2]	−10·0

TABLE 3

Reduction of hept-2-en-4-yn-1-ol

$LiAlH_4$		Glucofuranose derivative		Hept-3-en-4-yn-1-ol		Hepta-3,4-dien-1-ol			
						Yield		B.p.(°C) [mmHg]	$[\alpha]_D^{20}$(°)
g	mol	g	mol	g	mol	g	%		
3·5	0·092	23·3	0·067	3·7	0·033	2·4	64	79—81 [6]	−2·8
4·0	0·105	23·3	0·067	3·7	0·033	2·6	69	80—81 [6]	−1·2
4·5	0·118	23·3	0·057	3·7	0·033	2·9	76	74 [5]	−2·7
3·5	0·092	23·3	0·067	1·9	0·017	1·3	68	60 [3]	−8·7
3·5	0·092	23·3	0·067	1·9	0·017	1·4	73	56 [1·2]	−8·9

TABLE 4

Reduction of non-2-en-4-yn-1-ol

$LiAlH_4$		Glucofuranose derivative		Non-2-en-4-yn-1-ol		Nona-3,4-dien-1-ol			
						Yield		B.p.(°C) [mmHg]	$[\alpha]_D^{20}$(°)
g	mol	g	mol	g	mol	g	%		
3·5	0·092	23·3	0·067	2·3	0·017	1·7	74	81—82 [1·2]	−8·3
4·0	0·105	23·3	0·067	2·3	0·017	1·7	74	80—82 [1·3]	−7·4

TABLE 5

Reduction of 5-phenylpent-2-en-4-yn-1-ol

$LiAlH_4$		Glucofuranose derivative		5-Phenylpent-2-en-4-yn-1-ol		5-Phenylpenta-3,4-dienol			
						Yield		B.p.(°C) [mmHg]	$[\alpha]_D^{20}$(°)
g	mol	g	mol	g	mol	g	%		
3·5	0·092	23·3	0·067	2·6	0·017	1·0	37	102 [0·05]	−15·4
8·0	0·210	46·6	0·133	5·2	0·033	2·3	44	114 [1·5]	−15·9

experiments, in which the quantities of reactants were varied, were carried out by this general method (see Table 2).

(*b*) *Monosaccharide added at end of reduction.* A solution of hex-2-en-4-yn-1-ol (10 g, 0·01 mol) in ether (50 ml) was added dropwise over 0·5 h at room temperature with stirring to a standardised solution of lithium aluminium hydride (0·015 mol) in ether (59·0 ml) and the mixture was heated under reflux for 2 h. A solution of analytically pure 3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose [2] (5·3 g, 0·015 mol) in ether (50 ml) was then added dropwise over 0·5 h and the refluxing was continued for a further 2 h. The complex was decomposed by pouring into 10% sulphuric acid (150 ml); the mixture was extracted with ether (3 × 100 ml) and the extracts were washed with water (2 × 50 ml), dried, and evaporated. Distillation gave hexa-3,4-dien-1-ol (0·4 g, 40%), $[\alpha]_D^{25}$ −8·2° (neat), b.p. 60° at 4 mmHg, identical (i.r. spectrum) with the foregoing sample.

Hepta-3,4-dien-1-ol.—Hept-2-en-4-yn-1-ol was reduced as in (*a*) above to (−)-hepta-3,4-dien-1-ol, $\nu_{max.}$ 3400—3300 (OH) and 1950 cm^{-1} (C=C=C), identical with an authentic sample; G.l.c. t_R 8·5 min (silicone oil; 148°) (see Table 3).

Nona-3,4-dien-1-ol.—Non-2-en-4-yn-1-ol was similarly reduced to (−)-nona-3,4-dien-1-ol (Found: C, 76·5; H, 11·3. $C_9H_{16}O$ requires C, 77·1; H, 11·4%), $\nu_{max.}$ 1950 (C=C=C) and 1040—1030 cm^{-1} (C–O), g.l.c. t_R 18 min (silicone oil; 148°) (see Table 4).

5-Phenylpenta-3,4-dien-1-ol.— 5-Phenylpent-2-en-4-yn-1-ol was similarly reduced to give (−)-5-phenylpenta-3,4-dien-1-ol, $\nu_{max.}$ 3400—3300 (OH), 1940 (C=C=C), 1695 and 1485 (aromatic C=C), 1060—1020 (C–O), and 755 and 680 cm^{-1} (aromatic monosubstitution), was identical with an authentic sample [5] (see Table 5).

(−)-*Nona-3,4-diene-6,8-diyn-1-ol* [(−)-*Marasin*].—(*a*) A solution of pure 3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose [2] (11·2 g, 0·032 mol) in ether (50 ml) was added dropwise with stirring to lithium aluminium hydride (1·67 g, 0·044 mol) in ether (50 ml) and the mixture was heated under reflux for 2 h. The solution was then allowed to cool to room temperature and a solution of non-2-ene-4,6,8-triyn-1-ol [5] (1 g) in ether (60 ml) was added dropwise; stirring was continued for 2 h at room temperature. The complex was decomposed by pouring into 10% sulphuric acid (140 ml) with rapid stirring. The mixture was extracted with ether (3 × 100 ml) and the extracts were washed with water (3 × 100 ml) and dried. The ethereal solution was repeatedly evaporated to 50 ml after addition of n-pentane (100 ml). It was then chromatographed on Woelm acid alumina (200 g) deactivated with water (6 ml, 3%) and eluted with n-pentane (5 × 400 ml) and then ether–n-pentane (1 : 4; 20 × 400 ml); (−)-marasin (0·12 g, 12%) was eluted in fractions 12—16 (detected by u.v. scanning). Fractions 12—16 were combined and evaporated to 50 ml, and rechromatographed on silica (400 g) impregnated with boric acid (120 ml of 0·1M-solution). Elution with n-pentane (10 × 100 ml) yielded (−)-marasin (0·12 g, 12%), $\lambda_{max.}$ 208 (ε 51,000), 224 (3200), 107 (5000), 249·5 (8900), 263 (14,100), and 278 nm (12,500), $\nu_{max.}$ 3300, 2200, and 1960 cm^{-1}. Evaporation to 20 ml without heating gave a solution with $[\alpha]_D^{20}$ −26·6° (*c* 0·6 in n-pentane). Further evaporation to 2 ml gave a solution with $[\alpha]_D^{20}$ −20·3 (*c* 0·6 in n-pentane). T.l.c. showed one spot, R_F 0·6 (brown).

(*b*) In an attempt to remove traces of monosaccharide impurities by hydrolysis, marasin was prepared as in (*a*) by use of monosaccharide containing 1% impurity. Methanol (100 ml) was added to the ethereal solution of marasin and the solution was evaporated to 100 ml without heating. Concentrated hydrochloric acid (60 ml) was then added and the solution was stirred for 2 h at room temperature. After addition of water (400 ml) the mixture was extracted with ether (5 × 100 ml), and the combined extracts were dried. Repeated evaporation to 50 ml with addition of n-pentane followed by chromatography on alumina as in (*a*) yielded pure marasin (0·1 g, 10%), $\lambda_{max.}$ 208 (ε 51,000), 224 (3200), 327 (5000), 249·5 (8900), 263 (14,100), and 278 nm (12,500), $[\alpha]_D^{20}$ −0·00°. T.l.c. showed one spot, R_F 0·6 (brown). Four experiments under similar acid conditions gave only optically inactive marasin.

Dec-2-ene-4,6,8-triyn-1-ol.—Copper(I) chloride (1·66 g, 0·016 mol), hydroxylamine hydrochloride (0·02 g), dimethylformamide (40 ml), and aqueous 70% ethylamine (2·9 ml, 0·032 mol) were placed in a dropping funnel under oxygen-free nitrogen and shaken for 0·5 min. The light green suspension was then added in one portion to a solution of penta-1,3-diyne [6] under nitrogen and the mixture was cooled in an ice-bath. A bright yellow precipitate formed. After 0·5 min a solution of 5-bromopent-2-en-4-yn-1-ol (8·05 g, 0·05 mol) in dimethylformamide (30 ml) was added in one portion. The mixture was stirred under nitrogen at 0° for 2 h. The complex was then decomposed by addition of potassium cyanide (30 g) in water (150 ml) and extracted with ether (3 × 200 ml). The extracts were washed with water (2 × 100 ml), 2·5N-hydrochloric acid (2 × 100 ml), and water (3 × 200 ml) and dried. The solution was repeatedly evaporated to 60 ml without heating with addition of n-pentane, and chromatographed on Woelm acid alumina (200 g) deactivated with water (6 ml, 3%). The column was eluted with n-pentane (6 × 400 ml) and then ether–n-pentane (1 : 4; 20 × 400 ml). Fractions 13—16 contained dec-2-ene-4,6,8-triyn-1-ol (2·05 g, 28·6%), $\lambda_{max.}$ (ε 99,500), 230 (67,000), 241·5 (87,000), 272 (6800), 288·5 (12,500). 307·5 (17,000), and 329 nm (12,000).

(−)-*Deca-3,4-diene-6,8-diyn-1-ol*[(−)-9-*Methylmarasin*].—A solution of analytically pure 3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose [2] (12·36 g, 0·035 mol) in ether (50 ml) was added dropwise with stirring to a standardised solution of lithium aluminium hydride (0·035 mol) in ether (57·6 ml) over 0·5 h and the mixture was heated under reflux for 2 h. The solution was then allowed to cool to room temperature and dec-2-ene-4,6,8-triyn-1-ol (1·05 g, 0·007 mol) in ether (60 ml) was added over 0·5 h; stirring was continued at room temperature for a further 2 h. Work-up and chromatography as described for marasin gave 9-methylmarasin (0·15 g, 10%), $\lambda_{max.}$ 208 (ε 56,000), 224·5 (3900), 237 (6500), 250·5 (12,100), 264 (16,000) and 280 nm (12,900). Evaporation to 20 ml gave a solution with $[\alpha]_D^{25}$ −11·3° (*c* 0·75 in n-pentane); further evaporation to 2 ml gave a solution with $[\alpha]_D^{25}$ −11·013°; t.l.c. showed one spot, R_F 0·6 (brown).

7-Phenylhept-2-ene-4,6-diyn-1-ol.—Copper(I) chloride (1·65 g, 0·016 mol), hydroxylamine hydrochloride (0·02 g), dimethylformamide (20 ml), and aqueous 70% ethylamine (2·68 ml, 0·033 mol) were placed in a dropping funnel under oxygen-free nitrogen and shaken for 0·5 min. The light green suspension was then added in one portion to a solution

[5] S. R. Landor, E. S. Pepper, and J. P. Regan, *J. Chem. Soc.* (*C*), 1967, 189.

[6] J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1952, 1993.

of phenylacetylene (10·2 g, 0·1 mol) in dimethylformamide (40 ml) under nitrogen at 0°. A bright yellow precipitate formed. After 0·5 min a solution of 5-bromopent-2-en-4-yn-1-ol (8·05 g, 0·05 mol) in dimethylformamide (30 ml) was added in one portion and the solution turned a light green colour. The mixture was stirred under nitrogen at 0° for 2·5 h and the complex was then decomposed by addition of potassium cyanide (30 g) in water (150 ml). The mixture was extracted with ether (3 × 200 ml) and the extracts were washed with water (2 × 200 ml), dried, repeatedly evaporated to 50 ml with addition of n-pentane, and chromatographed on Spence type H alumina (100 g) deactivated with aqueous 10% acetic acid (5 ml). Elution with n-pentane and then ether–n-pentane (1 : 4) gave 7-phenylhept-2-ene-4,6-diyn-1-ol (5·8 g, 70%), $\lambda_{max.}$ 210 (ε 55,000), 230 (37,800), 240 (36,000), 252 (27,000), 265 (15,000), 299 (31,800), and 319 nm (25,600).

(−)-7-*Phenylhepta*-3,4-*dien*-6-*yn*-1-*ol*.—A solution of pure 3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose [2] (8·5 g, 0·024 mol) in ether (25 ml) was added dropwise with stirring over 0·5 h to a standardised solution of lithium aluminium hydride (0·024 mol) in ether (41 ml) and the mixture was heated under reflux with stirring for 2 h. The solution was then allowed to cool to room temperature and a solution of 7-phenylhept-2-ene-4,6-diyn-1-ol (0·9 g, 0·005 mol) in ether (50 ml) was added over 0·5; stirring was continued for 2 h at room temperature. The complex was then decomposed by pouring into 10% sulphuric acid (200 ml) with rapid stirring, and the mixture was extracted with ether (3 × 100 ml). The combined extracts were washed with water, dried, repeatedly evaporated to 50 ml with addition of n-pentane, and chromatographed on Spence type H alumina (100 g) deactivated with aqueous 10% acetic acid (5 ml). Elution with n-pentane (4 × 200 ml) and then ether–n-pentane (1 : 4; 6 × 200 ml) gave 7-phenylhepta-3,4-dien-6-yn-1-ol fractions 8—10 (u.v. scanning); these were combined and evaporated without heating to 60 ml and chromatographed on silica gel (200 g) impregnated with boric acid (60 ml of 0·1M-solution) giving 7-phenylhepta-3,4-dien-6-yn-1-ol (0·13 g, 14·4%), $\lambda_{max.}$ 205 (ε 41,500), 257 (13,600), 273·5 (19,300), and 288 nm (14,800), λ_{sh} 218 nm (ε 29,000), $\nu_{max.}$ 3300 (OH) and 1950 cm^{-1} (C=C=C). Evaporation to 20 ml gave a solution with $[\alpha]_D^{25}$ −3·1° (*c* 0·65 in n-pentane), and further evaporation to 2 ml gave a solution with $[\alpha]_D^{20}$ −2·8°; t.l.c. gave one spot, R_F 0·75 (yellow).

(−)-9,9-*Dimethylnona*-3,4-*dien*-6-*yn*-1-*ol*.—A solution of pure 3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose [2] (9 g, 0·026 mol) in ether (50 ml) was added dropwise with stirring over 0·5 h to a standardised solution of lithium aluminium hydride (0·026 mol) in ether (62·5 ml) and the mixture heated under reflux with stirring for 2 h. The solution was allowed to cool to room temperature, a solution of 8,8-dimethylnon-2-ene-4,6-diyn-1-ol [5] (1·67 g, 0·01 mol) in ether (50 ml) was added over 0·5 h, and stirring was continued at room temperature for 2 h. The complex was then decomposed by pouring into 10% sulphuric acid (200 ml) with rapid stirring. The mixture was extracted with ether (3 × 150 ml) and the combined extracts were washed with water (2 × 50 ml) and dried. Distillation gave (−)-8,8-*dimethylnona*-3,4-*dien*-6-*yn*-1-*ol* (0·55 g, 32%), b.p. 79° at 2 × 10^{-3} mmHg (Found: C, 80·5; H, 9·8. $C_{11}H_{16}O$ requires C, 80·6; H, 9·8%); $\lambda_{max.}$ 219 nm (ε 14,690), $\nu_{max.}$ 3300 (OH) and 1600 cm^{-1} (C=C=C), $[\alpha]_D^{25}$ −12·5° (neat).

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