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THE NEOFLAVANOID GROUP OF NATURAL PRODUCTS—III

THE SYNTHESIS AND NUCLEAR MAGNETIC RESONANCE SPECTRA OF THE DALBERGIONES

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Abstract—The synthesis of the racemates (±)-4-methoxydalbergione (IIIa) and (±)-3,4-dimethoxydalbergione (IIIb) has been achieved by Claisen rearrangements of the corresponding cinnamyl ethers (Ia and Ib) followed by Fremy's salt oxidation. These syntheses are based upon the biosynthetic schemes examined in Part II of this series.

The NMR spectra of the dalbergiones and their derivatives are discussed.

THE recognition of the neoflavanoids as a structurally interrelated group of natural products was discussed in Part I of this series,[1] and the dalbergiones (III) were considered to be typical members of this group. Speculations concerning the biosynthesis of the dalbergiones suggested that they may be regarded as products of a biosynthetic S_N2'-type alkylation of a phenolic or polyketide intermediate by a suitably activated cinnamyl unit such as cinnamyl pyrophosphate.[2] This suggestion is clearly recognized as one of several plausible pathways which require biosynthetic enquiry but these considerations did point the way to a simple synthesis of the dalbergiones involving alkylation of suitable phenols with cinnamyl bromide.

Normally the direct cinnamylation of phenols gives either O-cinnamyl ethers or C-cinnamyl phenols,[3] but the laboratory equivalent of the S_N2'-reaction discussed above is the formation of *o*-1-phenylallyl-phenols (II) by the Claisen rearrangement[4] of cinnamyl-phenyl ethers (I). This reaction sequence (I → II → III) has been used for the synthesis of the racemic (±)-4-methoxydalbergione (IIIa) and (±)-3,4-dimethoxy-dalbergione (IIIb) which correspond with the natural products.[1,2]

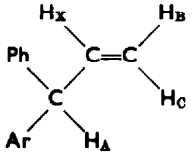
The Claisen rearrangement of the cinnamyl ether (Ia), achieved by heating it in dimethylaniline, yielded a mixture of two *ortho*-rearrangement products which, by study of their NMR spectra, were shown to have the structures (IIa and IVa). The phenol (IIa) by oxidation with Fremy's salt[5] yielded the quinone (IIIa) which had an

[1] W. B. Eyton, W. D. Ollis, I. O. Sutherland, O. R. Gottlieb, M. Taveira Magalhães and L. M. Jackman, Part I of this series, *Tetrahedron* **21**, 2683 (1965).
[2] W. B. Eyton, W. D. Ollis, M. Fineberg, O. R. Gottlieb, I. Salignac de Souza Guimarães and M. Taveira Magalhães, Part II of this series, *Tetrahedron* **21**, 2697 (1965).
[3] C. D. Hurd and L. Schmerling, *J. Amer. Chem. Soc.* **59**, 107 (1937).
[4] L. Claisen and E. Tietze, *Ber. Dtsch. Chem. Soc.* **58**, 275 (1925); D. S. Tarbell, *Organic Reactions* **2**, 1 (1944).
[5] H. J. Teuber and G. Jellinek, *Chem. Ber.* **85**, 95 (1952); H. J. Teuber and W. Rau, *Chem. Ber.* **86**, 1036 (1953).

TABLE 1. UV ABSORPTION SPECTRA λ_{max} mμ (ε_{max}) IN ETHANOL

IIc	227 (13,680)	275 (2,130)
VIIa	226 (13,420)	277 (1,970)
IIe		273 (1,670)
VIIb		272 (1,520)
IVc		272 (2,120)
VIII		272 (1,890)
Vb	254 (22,370)	292 (2,100)
IX	261 (840)	267 (780)

TABLE 2. CHEMICAL SHIFTS (τ IN $CDCl_3$ SOLUTION) OF ABCX PROTONS IN COMPOUNDS OF THE GENERAL TYPE (XI)



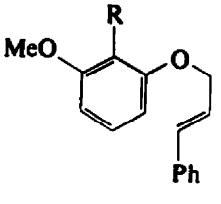
Ar = aryl ring or quinonoid residue

XI

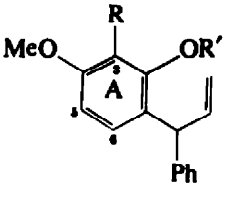
	H_A	H_B	H_C	H_X
R-4-Methoxydalbergione (IIIa)[1]	5·07	4·75	5·02	3·86
R-3,4-Dimethoxydalbergione (IIIb)[8]	5·17	4·78	5·05	3·90
S-3,4′-Dimethoxydalbergione (IIIc)[1]	5·18	4·82	5·08	3·94
(IIb)	5·06	4·74	5·02	3·64
(IIc)	5·15	4·83	5·04	3·69
(IIe)	5·18	4·76	5·04	3·69
(IVb)	4·49	4·68	4·85	3·43
(IVc)	4·70	4·78	4·83	3·51
(VIa)[1]	5·22	4·80	5·10	3·78
(VIb)[8]	5·17	4·73	5·03	3·75

IR spectrum in chloroform solution identical with that of natural R-4-methoxydalbergione. The quinone (IIIa) was identical in all respects[1] with the racemate prepared by crystallization of a mixture of equal amounts of the natural R- and S-4-methoxydalbergiones.

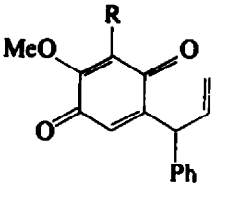
A similar series of reactions starting from the cinnamyl ether (Ib) gave the racemic



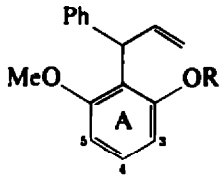
Ia R = H
Ib R = OMe



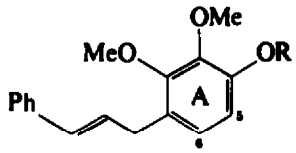
IIa R = R′ = H
IIb R = H, R′ = D
IIc R = H, R′ = Ac
IId R = OMe, R′ = H
IIe R = OMe, R′ = Ac



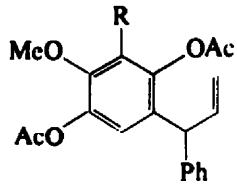
IIIa R = H
IIIb R = OMe
IIIc R = H; Ph replaced by *p*-methoxyphenyl



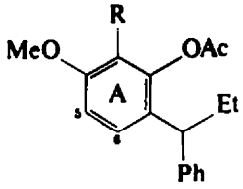
IVa R = H
IVb R = D
IVc R = Ac



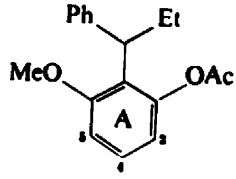
Va R = H
Vb R = Ac



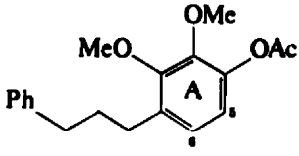
VIa R = H
VIb R = OMe



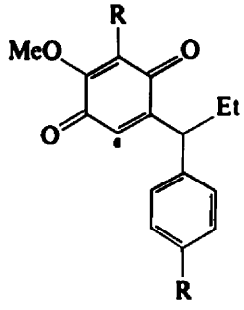
VIIa R = H
VIIb R = OMe



VIII



IX

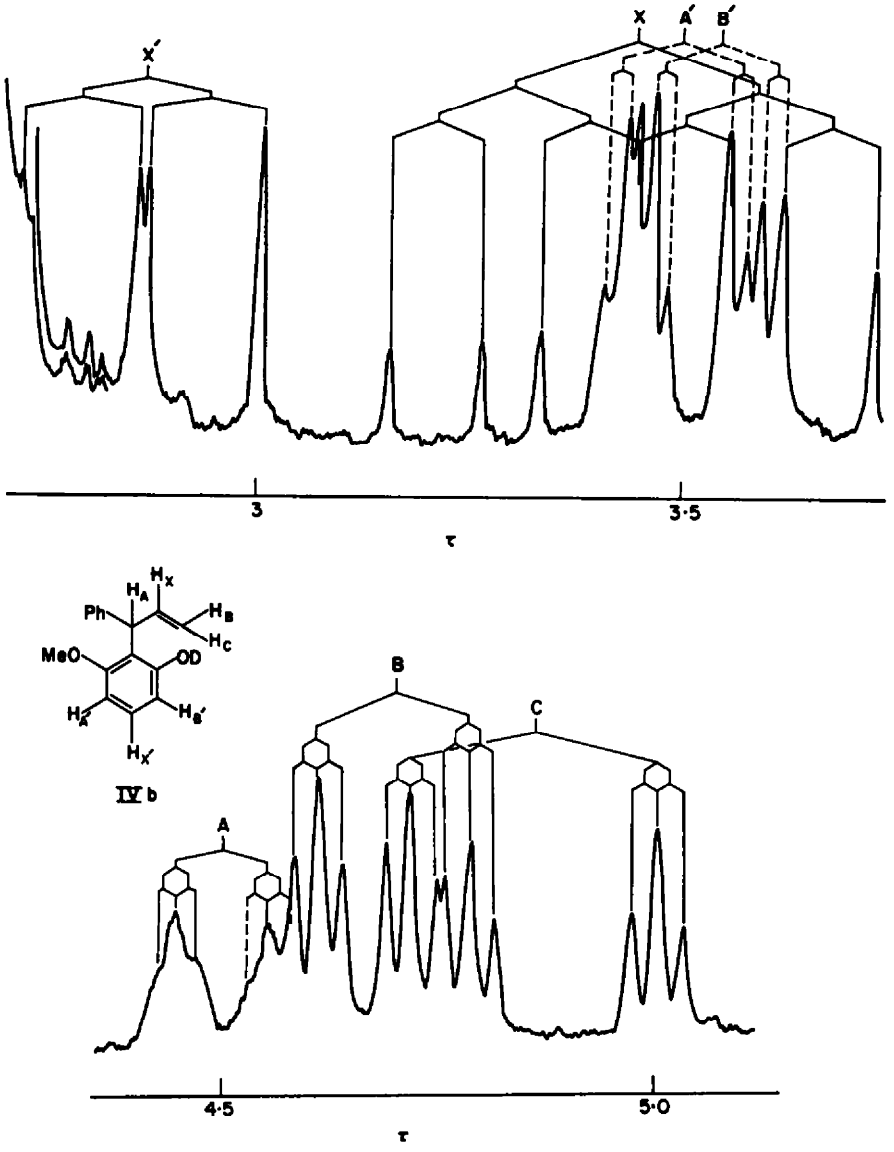


Xa R = H
Xb R = OMe

quinone (IIIb) corresponding to the natural R-3,4-dimethoxydalbergione.[2] In this case the Claisen rearrangement also yielded two products of which one was the required *ortho*-product (IId), whereas the other was the *para*-isomer (Va) with a cinnamyl side chain. The structure of these compounds was readily deduced from their NMR spectra (see Table 2) in conjunction with their UV (Table 1) and IR spectra (Experimental).

Nuclear magnetic resonance spectra of phenylallyl derivatives

In Part I of this series, the NMR spectra of the dalbergiones and their derivatives were summarized, but no detailed analysis of the multiplets associated with the four protons located in the >CH—CH=CH_2 residue was given. Later it was found that these NMR spectra yielded to first-order analysis and this provided unambiguous evidence for the detailed structure of the non-aromatic portion of the dalbergione structures.

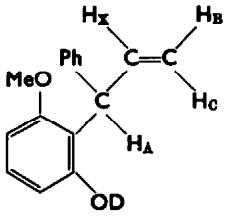


IV b

FIG. 1. First order analysis of ABCX and A'B'X' components of the NMR spectrum ($CDCl_3$ solution + D_2O) of 3-phenyl-3-(2'-hydroxy-6'-methoxyphenyl)-propene (IVb). See Fig. 2 and Table 3 for chemical shifts and coupling constants.

The spectrum (Figs 1 and 2) of the Claisen rearrangement product (IVb) shows, after deuteration of the phenolic hydroxyl group, those features characteristic of the dalbergione type structure. The coupling patterns associated with the A'B'X' system[6] of the three aromatic A-ring protons and the ABCX system[6] associated with the

[6] J. A. Pople, W. G. Schneider and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance*, McGraw-Hill (1959). J. D. Roberts, *An Introduction to the Analysis of Spin–Spin Splitting in Nuclear Magnetic Resonance*, W. A. Benjamin (1961).



IVb

Chemical shifts τ		Coupling constants c/s	
H_A	4·49	J_{AX}	6·3
H_B	4·68	J_{BX}	10·5
H_C	4·85	J_{CX}	17·2
H_X	3·43	J_{AB}	1·7
		J_{AC}	1·7
		J_{BC}	1·7

FIG. 2. The chemical shifts and coupling constants deduced by first order analysis of the spectra given in Fig. 1.

$>CH—CH=CH_2$ side chain may be analysed in terms of the *apparent* coupling constants. Although second order analysis is normally required for accurate determination of chemical shifts and coupling constants in an ABCX system, first order treatment in this case reveals the major coupling constants in the $>CH—CH=CH_2$ grouping and permits the assignment of chemical shifts to the four protons.

The chemical shifts and *apparent* coupling constants for the indicated protons in the formula (IVb) are summarized in Fig. 2. Signs have not been allocated to the coupling constants, but this does not affect this type of analysis. It is clear that the assignments are fully acceptable. The signals due to the benzylic proton A show a broadening in addition to the multiplicities dictated by the above couplings. This is presumably due to an additional long-range coupling between the benzylic proton H_A and the *ortho*-protons of the phenyl group.

The 1,2,3-arrangement of the three protons on the oxygenated ring of (IVb) clearly follows from the NMR spectra (Fig. 1).

An analysis was made in a similar manner of the NMR spectra of other compounds listed in Table 2. The apparent coupling constants were very close to those listed for the compound IVb and these are not therefore included in Table 2. The chemical shifts of the protons forming the ABCX system are those given by first order analysis. It was noticed that considerable deviation from intensities to be expected by such an analysis was shown in certain spectra when τ_A approached τ_C.

The chemical shifts and multiplicities (Table 3) of the aromatic ring-A protons were in full accord with the indicated structures. The structures and NMR spectra of the dihydrodalbergiones and their derivatives, in which the vinyl group has been reduced to an ethyl group, have already been given preliminary consideration.[1] The NMR spectra of these compounds (Table 4) show the triplet, quintet and triplet signals to be expected from the >CH—, $—CH_2—$ and $—CH_3$ groups associated with the $>CH—CH_2—CH_3$ structure, and the coupling constants are approximately equal ($J \sim 7$ c/s). Just as with the dalbergiones, the dihydrodalbergiones (Xa and Xb) also show a long range coupling between the benzylic proton of the side chain and the proton in position 6 of the quinonoid residue.

TABLE 3. CHEMICAL SHIFTS (τ IN $CDCl_3$ SOLUTION) OF THE RING-A AROMATIC PROTONS

	3-H	4-H	5-H	6-H
IIb	3·61 (d, J ~ 2·4)		3·52 (qu, J ≃ 8·2, 2·4)	2·98 (d, J = 8·2)
IIc	3·30 (d, J = 2·5)		3·22 (qu, J = 9·4, 2·5)	2·79*
IIe			3·18 (d, J = 8·8)	3·07 (d, J = 8·8)
IVb	3·48 (qu, J = 7·7, 1·3	2·84 (qu, J = 8·4, 7·7)	3·53 (qu, J = 8·4, 1·3)	
IVc	3·19 (qu, J = 8·2, 1·3)	2·71*	3·23 (qu, J = 8·2, 1·3)	
Vb			3·18 (d, J = 8·5)	3·01 (d, J = 8·5)
VIIa	3·35 (d, J = 2·6)		3·17 (qu, J = 2·6, 8·6)	2·68 (d, J = 8·6)
VIIb			3·16 (d, J = 8·5)	2·95 (d, J = 8·5)
VIII	3·22 (qu, J = 8·4, 1·4)	2·73*	3·29 (qu, J = 8·0, 1·4)	
IX			3·20 (d, J = 8·5)	3·06 (d, J = 8·5)

The location of the protons is indicated in the appropriate structural formula and for ease of comparison systematic numbering has not been used.

d = doublet, t = triplet, qu = quartet, qi = quintet. The coupling constants J are given in c/sec.

* Details obscured by phenyl resonances.

TABLE 4. CHEMICAL SHIFTS (τ IN $CDCl_3$ SOLUTION) OF SIDE-CHAIN PROTONS IN $>CH_{(A)}—CH_{2_{(B)}}—CH_{2_{(C)}}$ GROUPS

	A	B	C
VIIa*	6·08	7·98	9·10
VIIb	6·10	7·98	9·10
VIII*	5·37	7·78	9·12
Xa[1]	5·96	8·12	9·12
Xb[2]	6·01	8·13	9·12

Nuclear magnetic resonance spectra of cinnamyl derivatives

Our studies of the Claisen rearrangement of O-cinnamyl phenyl ethers provided us with a number of related compounds and the study of their NMR spectra is of interest in connection with our studies of the natural occurrence of benzylstyrenes.[2,7] The signals associated with the $—CH_2—CH\overset{t}{=}CH—$ part of their structure are not analysable by first order methods, but treatment as an ABX_2[8] system gave satisfactory agreement between the observed and calculated spectra using the τ and J values given in Table 5.

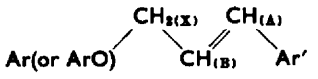
The ABX_2 component of NMR spectra for these cinnamyl derivatives are of two types (Figs 3a and 3b). The cinnamyl ethers for which $\delta_{AB} \simeq J_{AB}$ give calculated spectra of the type 3a, whereas the benzylstyrenes for which $\delta_{AB} \simeq \frac{1}{2}J_{AB}$ give calculated spectra of the type 3b.

* These two compounds were not characterized by analysis but their structures follow from their formation by catalytic hydrogenation of compounds of known structure and their ultra-violet (Table 1) and nuclear magnetic resonance spectra (Table 4).

[7] M. Gregson, W. D. Ollis and O. R. Gottlieb, forthcoming publication.

[8] P. L. Corio, *Chem. Rev.* **60**, 363 (1960); A. D. Cohen and N. Sheppard, *Proc. Roy. Soc.* **A252**, 488 (1959).

TABLE 5. CHEMICAL SHIFTS (τ IN $CDCl_3$ SOLUTION) AND COUPLING CONSTANTS (J c/s) FOR THE ABX_2 SYSTEM IN CINNAMYL COMPOUNDS (XII)



(XII)

	τ_A	τ_B	τ_X	J_{AB}	J_{AX}	J_{BX}
p-HO—C_6H_4—CH_2—CH=CHPh[a]	3·54	3·64	6·56	+15·9	−1·8	+6·9
Vb	3·48	3·62	6·45	+16·1	−1·5	+6·7
Ia	3·27	3·58	5·36	+16·05	−1·0	+5·7
Ib	3·18	3·49	5·20	+16·25	−0·9	+5·7

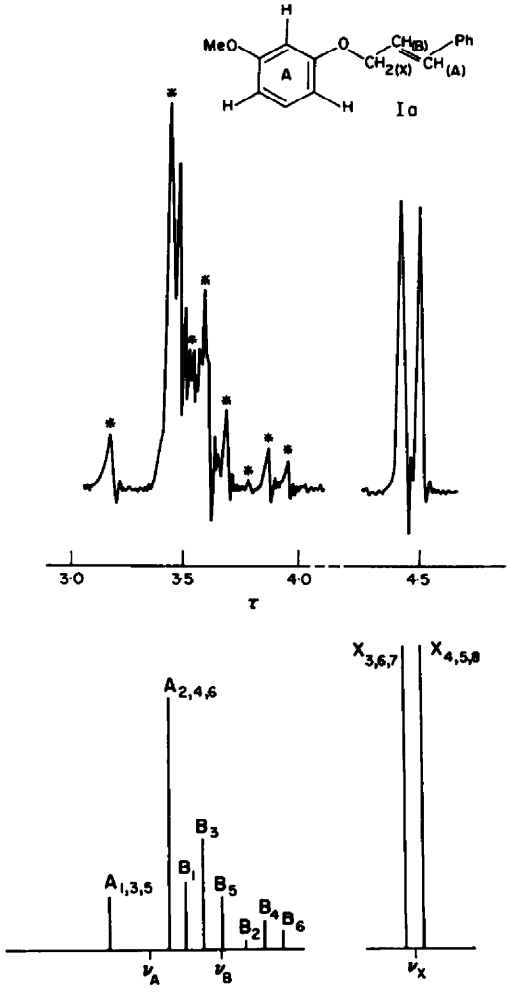


FIG. 3A. The observed and calculated (J_{AB} = 16·05 c/s and δ_{AB} = 19·06 c/s) ABX_2 component of the NMR spectrum of 3-cinnamyloxy-methoxybenzene (Ia).

The characteristic feature of this spectrum, in contrast with Fig. 3B, is that the X_2 protons are associated with a simple doublet.

* The asterisked lines are associated with the A and B protons of the ABX_2 system. These lines are superimposed upon the signals due to the *three* aromatic protons indicated on ring A.

[a] Phenol and cinnamyl bromide gave, according to the method of Claisen [*Liebig's Ann.* **442**, 234 (1925) as modified by Elkobaisi and Hickinbottem *J. Chem. Soc.* 2431 (1958)], a mixture of *o*- and *p*-cinnamylphenol.

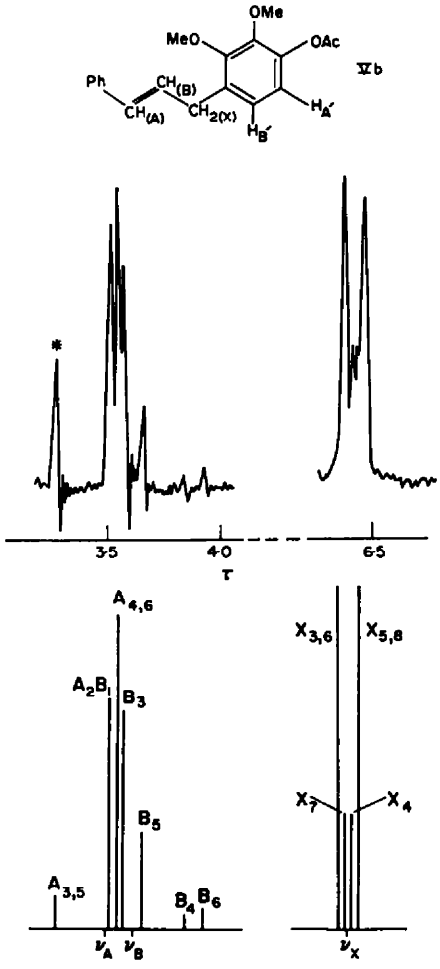


FIG. 3B. The observed and calculated (J_{AB} = 16·1 c/s and δ_{AB} = 7·35 c/s) ABX_2 component of the NMR spectrum of 2,3-dimethoxy-4-cinnamylphenyl acetate (Vb).

The characteristic features of this type of ABX_2 spectrum are (a) the additional signals associated with the X_2 doublet and (b) the intensity relationships shown by the signals associated with protons A and B.

* This signal in the observed spectrum is composite and is due to the $A_{3,5}$ component due to proton A and the high field signal associated with the doublet (τ 3·18; J = 8·5 c/s) due to proton A'.

EXPERIMENTAL

3-*Cinnamyloxy-methoxybenzene* (Ia). Resorcinol monomethyl ether (5·00 g), cinnamyl bromide (8·21 g) and anhydrous K_2CO_3 (8·0 g) were stirred in acetone (25 ml) for 15 hr at room temp and then filtered. The filtrate yielded an oil which was dissolved in ether (100 ml), shaken with 1 N NaOH (2 × 50 ml), washed, dried and evaporated to give 3-*cinnamyloxy-methoxybenzene* (Ia) as an oil (8·35 g; 86%) which was distilled (135–155°/0·1 mm). (Found: C, 79·90; H, 6·71; OMe, 13·22. $C_{16}H_{16}O(OMe)$ requires: C, 79·97; H, 6·71; OMe, 12·9%.)

3-*Cinnamyloxyveratrole* (Ib). Pyrogallol-1,2-dimethyl ether (2·6 g), cinnamyl bromide (3·4 g), and anhydrous K_2CO_3 (3·5 g) in acetone (50 ml) similarly gave, after stirring for 60 hr, 3-*cinnamyloxyveratrole* (Ib) (4·4 g; 93%) as colourless needles, m.p. 69·5°, from light petroleum (b.p. 60–80°). (Found: C, 75·8; H, 6·65; OMe, 23·2. $C_{16}H_{15}O(OMe)_2$ requires: C, 75·5; H, 6·70; OMe, 23·0%.)

Claisen rearrangement of 3-*cinnamyloxy-methoxybenzene*

Formation of 3-*phenyl*-3-(2'-*hydroxy*-4'-*methoxyphenyl*)-*propene* (IIa) *and* 3-*phenyl*-3-(2'-*hydroxy*-6'-*methoxyphenyl*)-*propene* (IVa). 3-Cinnamyloxymethoxybenzene (6·5 g) in N,N-dimethylaniline (25 ml) was heated under reflux (N_2 atm.) for 20 min. After cooling the mixture was diluted with benzene (100 ml), shaken with 2 N HCl and extracted with 3% NaOH aq (12 × 50 ml portions). The alkaline extract was acidified and extracted with ether to give an oil which was shown to contain two major components by thin layer chromatography. Chromatography on silica (120 g) and elution with benzene–cyclohexane (9:1) gave 3-*phenyl*-3-(2'-*hydroxy*-4'-*methoxyphenyl*)-*propene* (IIa) as a

colourless oil (1·26 g) which was purified by distillation (110–140°/0·1 mm). (Found: C, 79·78; H, 6·62; OMe, 13·13. $C_{18}H_{18}O(OMe)$ requires: C, 79·97; H, 6·71; OMe, 12·9%.)

Elution with benzene gave a second fraction as a colourless oil (2·86 g, b.p. 110–140°/0·1 mm) which was identified (NMR spectrum) as 3-phenyl-3-(2′-hydroxy-6′-methoxyphenyl)-propene (IVa). (Found: C, 79·83; H, 6·74; OMe, 13·34. $C_{18}H_{18}O(OMe)$ requires: C, 79·97; H, 6·71; OMe, 12·9%.)

Claisen rearrangement of 3-*cinnamyloxyveratrole*

Formation of 3-*phenyl*-3-(2-*hydroxy*-3,4-*dimethoxyphenyl*)-*propene* (IId) *and* 2,3-*dimethoxy*-4-*cinnamyl*-*phenol* (Va). 3-Cinnamyloxyveratrole (500 mg) was heated under reflux (N_2 atm.) in N,N-dimethylaniline (2 ml) for 2 hr, then worked up as in the preceding experiment. The crude phenolic product (440 mg) was chromatographed on silica and elution with benzene gave two major components. The faster-moving fraction (0·15 g) was distilled (95–105°/3 × 10^{-2} mm) giving 3-*phenyl*-3-(2′-*hydroxy*-3′,4′-*dimethoxyphenyl*)-*propene* (IId) as a colourless oil (Found: C, 75·55; H, 6·7. $C_{18}H_{18}O(OMe)_2$ requires: C, 75·5; H, 6·7%.) The slower-moving fraction (0·11 g) was also distilled (85–95°/3 × 10^{-2} mm) giving 2,3-*dimethoxy*-4-*cinnamyl*-*phenol* (Va). (Found: C, 75·4; H, 6·7. $C_{18}H_{18}O(OMe)_2$ requires: C, 75·5; H, 6·7%.)

Acetylation of the products from the Claisen rearrangements

Formation of the acetates IIc, IIe, IVc and Vb. The phenols were acetylated in the usual way by treatment with excess acetic anhydride—pyridine and the following products were purified either by short-path distillation or by crystallization from light petroleum (b.p. 60–80°).

3-*Phenyl*-3-(2′-*acetoxy*-4′-*methoxyphenyl*)-*propene* (IIc), colourless oil, b.p. 80–90°/2 × 10^{-2} mm. (Found: C, 76·5; H, 6·6; OMe, 10·2. $C_{17}H_{16}O_2(OMe)$ requires: C, 76·6; H, 6·4; OMe, 11·0%.)

3-*Phenyl*-3-(2′-*acetoxy*-6′-*methoxyphenyl*)-*propene* (IVc), m.p. 65·5°. (Found: C, 76·5; H, 6·6; OMe, 10·3. $C_{17}H_{16}O_2(OMe)$ requires: C, 76·6; H, 6·4; OMe, 11·0%.)

3-*Phenyl*-3-(2′-*acetoxy*-3′,4′-*dimethoxyphenyl*)-*propene* (IIe), m.p. 73·5°. (Found: C, 72·94; H, 6.19; OMe, 18·80. $C_{17}H_{14}O_2(OMe)_2$ requires: C, 73·0; H, 6·45; OMe, 19·9%.)

2,3-*Dimethoxy*-4-*cinnamyl*-*phenyl acetate* (Vb), colourless oil, b.p. 105–115°/10^{-2} mm. (Found: C, 73·25; H, 6·65; OMe, 19·1. $C_{17}H_{14}O_2(OMe)_2$ requires: C, 73·06; H, 6·45; OMe, 19·9%.)

1-*Phenyl*-1-(2′-*acetoxy*-3′,4′-*dimethoxyphenyl*)-propane (VIIb). The Claisen rearrangement product (IId, 200 mg) was hydrogenated in methanol (10 ml) at atm. press. and room temp using pre-reduced Adam's PtO_2 catalyst. The oily product was acetylated directly using acetic anhydride and pyridine yielding the *acetate* (VIIb) as colourless needles, m.p. 82·5°, from light petroleum, b.p. 60–80°. (Found: C, 72·55; H, 7·00. $C_{19}H_{22}O_4$ requires: C, 72·6; H, 7·05%.)

1-*Phenyl*-3-(4-*acetoxy*-2,3-*dimethoxyphenyl*)-*propane* (IX). As in the preceding experiment, reduction and acetylation of the Claisen rearrangement product (Va) gave the acetate (IX) as a colourless oil (b.p. 125–135°/0·03 mm). (Found: C, 72·5; H, 7·25; OMe, 19·00. $C_{18}H_{20}O_2(OMe)$ requires: C, 72·6; H, 7·05; OMe, 19·7%.) NMR spectrum ($CDCl_3$): τ 2·68, 5H (Ph); τ 3·05 (d, J = 8·5 c/s), 1H, (H_6); τ 3·20 (d, J = 8·5 c/s) 1H, (H_5); τ 6·13, 3H, (OMe); τ 6·14, 3H, (OMe); $\tau \sim$ 7·3 (m), 4H, (benzylic CH_2)$_2$; τ 7·69, 3H, (OAc); $\tau \sim$ 8·1 (m) (isolated CH_2).

Racemic 4-*methoxydalbergione* (IIIa). 3-Phenyl-3-(2′-hydroxy-4′-methoxyphenyl)propene (IIa, 240 mg) in MeOH (40 ml) was added at room temp to a stirred aqueous solution (40 ml) of potassium nitrosyldisulphonate[6] (650 mg) and sodium acetate (250 mg) (N_2 atm.). After 15 min a flocculent yellow precipitate had separated. After the addition of water (50 ml), the mixture was stirred for a further 15 min, extracted with ether and this yielded a yellow solid which was purified by chromatography on silica (10 g). Elution of the major yellow band with benzene followed by crystallization from cyclohexane (6 ml) gave (±)-4-methoxydalbergione (122 mg; 44%) as yellow needles, m.p. 125°. (Found: C, 75·74; H, 5·59; OMe, 12·29. $C_{15}H_{11}O_2(OMe)$ requires: C, 75·57; H, 5·55; OMe, 12·2%.)

Racemic 3,4-*dimethoxydalbergione* (IIIb). Similarly 3-phenyl-3-(2′-hydroxy-3′,4′-dimethoxyphenyl)-propene (IId, 250 mg), MeOH (40 ml), potassium nitrosyldisulphonate (500 mg), sodium acetate (250 mg) and water (40 ml) gave after stirring for 3 hr (N_2 atm.) a mixture (160 mg) of quinone and unreacted phenol. Separation by repetitive thin layer chromatography on silica using benzene–chloroform (7:3) as the eluent eventually gave (±)-3,4-dimethoxydalbergione (IIIb, 49 mg) as orange needles, m.p. 42°, from light petroleum (b.p. 40–60°). (Found: C, 71·95; H, 5·65; OMe, 21·0. $C_{15}H_{10}O_2(OMe)_2$ requires: C, 71·82; H, 5·70; OMe, 22·05%.)