(CH_3SO_3H), 30768-66-2; **14**, 30771-61-0; TMP, 107-40-4; HCN, 74-90-8; HF, 7664-39-3.

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Arylnaphthalene Lignans. Synthesis of Justicidin E, Taiwanin C, Dehydrodimethylconidendrin, and Dehydrodimethylretrodendrin

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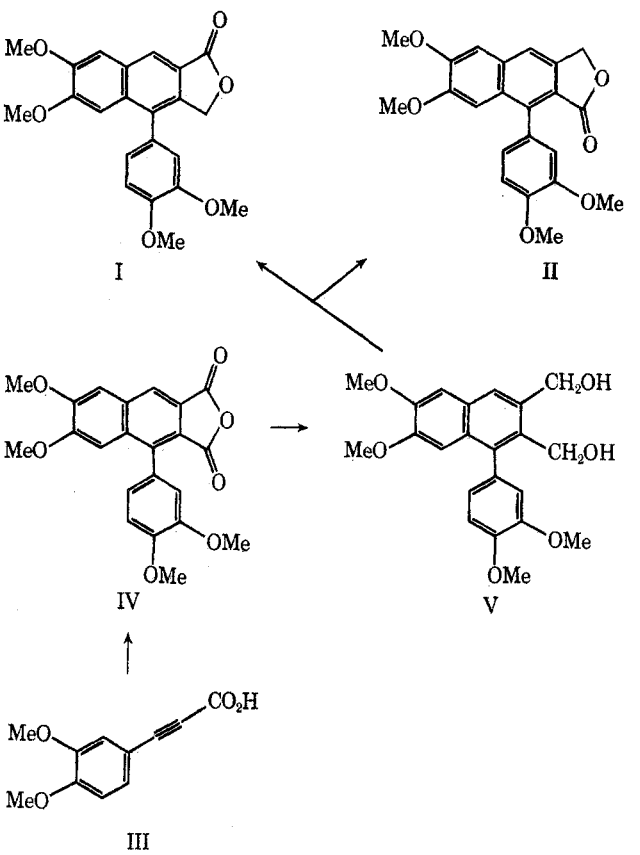
The naturally occurring lactones, justicidin E (VII) and taiwanin C (VI), have been synthesized by a short pathway starting from piperonylpropiolic acid. The tetramethoxy analogs, dehydrodimethylconidendrin (I) and dehydrodimethylretrodendrin (II), have been correspondingly obtained. Application of nmr spectroscopy to the structure elucidation of lignan arylnaphthalene lactones is discussed.

The arylnaphthalene lactones, dehydrodimethylconidendrin (I) and dehydrodimethylretrodendrin (II), although not yet reported to be naturally occurring, have been significant in the development of lignan chemistry, notably in the pioneering work of Haworth. Several interconversions with other classes of lignans have been achieved and syntheses of varying degree of complexity reported.[1-10]

We have sought to examine the generality of our recently reported synthesis[11] of helioxanthin by extension to a short convenient synthesis of dehydrodimethylconidendrin (I). Treatment of 3,4-dimethoxyphenylpropiolic acid (III) with acetic anhydride yielded 6,7-dimethoxy-1-(3′,4′-dimethoxyphenyl)naphthalene-2,3-dicarboxylic acid anhydride (IV),[2,12] which on reduction with lithium aluminum hydride in tetrahydrofuran solution gave the corresponding diol V. Treatment of V with silver carbonate–Celite (Fétizon's reagent)[13] resulted in smooth oxidation to a mixture of the lactones, dehydrodimethylconidendrin (I) and dehydrodimethylretrodendrin (II), in a ratio of approximately 9:1, as indicated by integration of the nmr spectrum of the lactone mixture. The lactone I was readily obtained by direct crystallization and the minor component, the lactone II, was isolated by thin layer chromatography of the crystallization mother liquors.

Although the methylenedioxy analogs VI and VII were first synthesized[14] in 1936 by the multistep procedures developed by Haworth for the tetramethoxy lactones I and II, they have only recently been reported to be of natural occurrence and no direct comparison, other than melting point proximity, has been made. Several crystalline extractives have been isolated[15] from the heartwood of *Taiwania cryptomerioides* Hayata and for one of these, taiwanin C, the structure 6,7-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid lactone (VI) has been proposed.[16] The isomeric structure VII has been proposed for a lactone, justicidin E, isolated as a piscicidal constituent from *Justicia procumbens*, and the conversion of (−)-parabenzlactone (VIII) to justicidin E is indicated in the same communication.[17]



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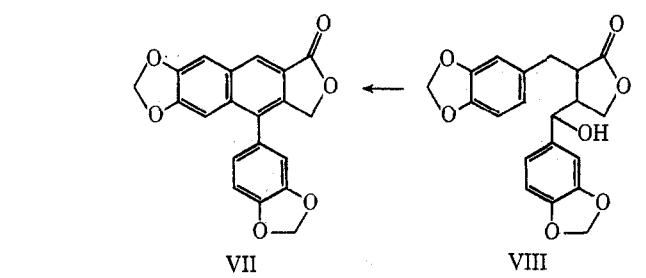
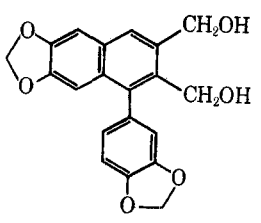
We have now prepared taiwanin C and justicidin E by the same simple pathway used for the tetramethoxy lactone I and II and with constants in excellent agreement with those reported for the natural products. 2,3-Bishydroxymethyl-6,7-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)naphthalene (IX), readily obtained from piperonylpropiolic acid by the action of acetic anhydride followed by reduction with lithium aluminium hydride and aluminium chloride in tetrahydrofuran,[18] was oxidized by silver carbonate–Celite to give a lactone mixture from which the major component, justicidin E (VII), was obtained by direct crystallization and the minor component, taiwanin C (VI), by thin layer chromatographic separation of the mother liquor residue.



VII VIII



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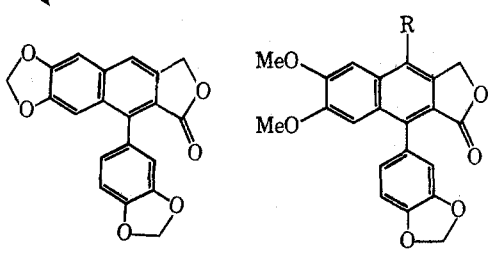

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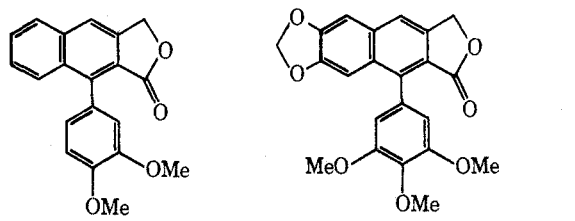
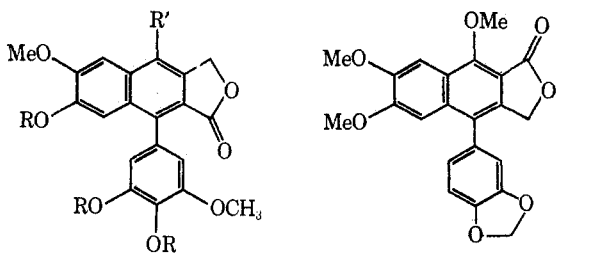


XI XII



XIII XIV

In the structure elucidation of naturally occurring lignan arylnaphthalene lactones, two diagnostic problems have in the past led to erroneous structure assignments. The first concerns whether the γ-lactone function is of the 1-aryl-3-naphthoic acid (*e.g.*, I and VII) or 1-aryl-2-naphthoic acid (*e.g.*, II and VI) types. These can now be clearly differentiated from pmr spectrum examination. A survey of the data available for compounds of established structure, initially by Horii[19] and supplemented herein, indicates that a lactone methylene group of type I, under the shielding influence of the benzenoid C ring, gives in deuteriochloroform solution a signal at δ 5.08–5.23, whereas that of type II is located at δ 5.32–5.54. Corroboration is also available for those lactones possessing a proton at C-4, the signal ascribed to this proton[10] in type I (strongly deshielded by the proximate carbonyl function) being at lower field (δ >8.0, typically at δ *ca.* 8.3) than that of type II (<8.0, typically at δ *ca.* 7.7).

The second problem is concerned with ascertaining, in those arylnaphthalenes possessing the frequently encountered veratrole moiety, whether the methoxyl groups are located in ring A (at C-6 and -7) or ring C (at C-3′ and -4′). The natural lactone, justicidin B (X, R = H),[20-22] has two methoxyl groups (δ 3.80 and 4.30) now known by degradation and synthesis evidence to be in ring A and which can be assigned respectively to C-7 and C-6, the more shielded group being closer to the influence of the aromatic ring C. Since dehydroanhydropicropodophyllin (XII) gives a six-proton signal at δ 3.83 and a three-proton signal at δ 3.96, the former can be attributed to the C-3′ (and -5′) methoxyl group and the latter to the C-4′ methoxyl group;[10] in agreement, the synthetic lactone[10] XI gives methoxyl signals at δ 3.87 (which can now be assigned to C-3′) and δ 3.98 (assigned to C-4′). With this data as an empirical basis for assignment of methoxyl resonance signals, noting particularly that the ring A pair exhibit a chemical shift difference, Δδ 0.23, and the ring C pair difference being Δδ 0.13, assignments could reliably be made for each of the four such functions in compounds I, II, IV, and V. From this background and other data available for arylnaphthalenes of known structure, the diagnostically useful range incorporated in Table I emerges.

Application of this information to the trimethyl ether of plicatinaphthalene (XIII, R = CH_3; R′ = H)[23] permits assignment of the reported methoxyl resonances, *viz.*, δ 4.02 (C-6), 3.77 (C-7), 3.82 (C-3′ and -5′), and 3.94 (C-4′) and to the tetramethyl ether derivative of plicatinaphthol (XIII, R = CH_3; R′ = OCH_3),[24] *viz.*, δ 4.06 (C-6), 3.78 (C-7), 3.84 (C-3′ and -5′), 3.97 (C-4′), and 4.13 (C-4). This value for the 4-methoxyl protons in XIII is in good agree-

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TABLE I

CHEMICAL SHIFT VALUES (δ) IN $CDCl_3$ SOLUTION

	Type I lactone (aryl-3-naphthoic acid)		Type II lactone (aryl-2-naphthoic acid)
Lactone methylene	5.08–5.23		5.32–5.54
H-4	*Ca.* 8.3		*Ca.* 7.7
4-OMe	*Ca.* 4.35		*Ca.* 4.1
Ring A (6,7-dimethoxyl)		Δ 0.21–0.28	
Ring C (3′,4′-dimethoxyl)		Δ 0.10–0.14	

ment with the value (δ 4.09) reported for justicidin A (X, R = OCH_3),[20] another type II lactone, and, in comparison with the values reported for 4-methoxy-substituted type I lactones, justicidin C (δ 4.37) and justicidin D (δ 4.33)[25] provide a further useful distinguishing feature.

Very recently, structure XIV has been proposed[26] for neojusticin B, a lignan isolated from *Justicia procumbens* var. *leucantha*. Evidence used in support of the location of the methylenedioxy group in ring C rather than A, namely the appearance of a mass spectrum fragment (*m/e* 121) characteristic of a methylenedioxyphenyl group, is not totally unequivocal. The reported signals at δ 3.83, 4.05, and 4.37 for three methoxyl groups, however, entirely supports the proposed structure. Thus, by reference to Table I, the last is as expected for a C-4 methoxyl group in a type II lactone, and the chemical shift difference ($\Delta\delta$ 0.22) locates the first two at C-7 and C-6 of ring A.

Experimental Section

Unless otherwise stated, the following generalizations apply. Melting points were determined either with a Gallenkamp or Fisher-Johns apparatus. Nmr spectra (δ) were determined for solutions in deuteriochloroform with tetramethylsilane as internal reference at 60 mc/sec.

Mass spectra were obtained at 70 eV using a AEI MS-12 instrument. Infrared spectra (λ, μ) were determined as KBr disks and ultraviolet spectra (λ, nm) in ethanol solution.

6,7-Dimethoxy-1-(3′,4′-dimethoxyphenyl)naphthalene-2,3-dicarboxylic Acid Anhydride (IV).—3,4-Dimethoxyphenylpropiolic acid (2 g, mp 144–145°) was added to acetic anhydride (10 ml), heated under reflux for 4 hr, and cooled. The tetramethoxy anhydride IV separated as a yellow solid (1.25 g): mp 302° (lit. mp 305–306°,[2] 316–317°[27]); λ 5.46 and 5.63 μ (anhydride); δ 3.84 s (7-OMe), 3.90 s (3′-OMe), 4.00 s (4′-OMe), 4.09 s (6-OMe), 6.93–7.25 complex m (four Ar H), 7.38 s (H-5), and 8.35 s (H-4); *m/e* 394 (M^+).

2,3-Bishydroxymethyl-6,7-dimethoxy-1-(3′,4′-dimethoxyphenyl)naphthalene (V).—The tetramethoxy anhydride (1.2 g) and excess lithium aluminium hydride were heated under reflux in tetrahydrofuran solution overnight and worked up in the usual way and the product was recrystallized from methanol to give the diol V as needles (350 mg): mp 189–190° (lit.[9] mp 188–189°); δ 3.03 br (two OH groups), 3.72 s (7-OMe), 3.83 s (3′-OMe), 3.97 s (4′ and 6-OMe), 4.62 s (C-2 CH_2OH), 4.88 s (C-3 CH_2OH), 6.78 s (H-8), 6.87–6.98 m (three Ar H), 7.13 s (H-5), and 7.68 s (H-4); *m/e* 384 (M^+).

Action of Silver Carbonate–Celite on 2,3-Bishydroxymethyl-6,7-dimethoxy-1-(3′,4′-dimethoxyphenyl)naphthalene (V).—The silver carbonate–Celite reagent (3 g) was added to a solution of the tetramethoxydiol (165 mg) in benzene (50 ml), and the mixture was heated under reflux for 5 hr, after removal of a small volume of solvent by distillation. It was then filtered and washed with ethyl acetate and benzene, and the combined filtrate and washings were evaporated to yield a residual orange gum (137 mg) which solidified upon addition of methanol. Two recrystallizations from this solvent gave 6,7-dimethoxy-1-(3′,4′-dimethoxyphenyl)-2-hydroxymethylnaphthalene-3-carboxylic acid lactone (I) (dehydrodimethylconidendrin) (32 mg) as tiny needles: mp 215–216° (lit.[2] mp 213–215°); λ 5.64 and 5.69 μ (lactone); λ 202 nm (ϵ 27,500), 224 (21,200), 229 (20,900), 257 (34,300), 319 (8000), and 350 infl (3000); δ 3.83 s (7-OMe), 3.89 s (3′-OMe), 3.99 s (4′-OMe), 4.04 s (6-OMe), 5.23 s (lactone methylene), 6.87–7.07 m (three Ar H), 7.15 s (H-8), 7.32 s (H-5), and 8.31 s (H-4); *m/e* 380 (M^+).

The mother liquors from the above recrystallizations (from two experiments) were combined, taken to dryness, and chromatographed on silica gel PF plates using petroleum ether (bp 38–60°)–ethyl acetate (1:1) with trace of acetic anhydride. The slower running zone (blue fluorescence under uv light) was eluted with ethyl acetate and crystallized once from methanol to give 6,7-dimethoxy-1-(3′,4′-dimethoxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid lactone (II) (dehydrodimethylretrodendrin) as pale yellow rhombs: mp 253–255° (lit. mp 254–255°,[2] 245–249°,[9] 251.5–253°[10]); λ 5.69 μ (lactone); λ 214 nm (ϵ 31,800), 221 (31,600), 250 infl (49,700), 258 (59,400), 286 (9200), 311 (10,900), and 346 (5200); δ 3.78 s (7′-OMe), 3.87 s (3′-OMe), 3.97 s (4′-OMe), 4.04 s (6-OMe), 5.37 d (J = 1.2 Hz) (lactone methylene), 6.93–7.03 m (three Ar H), 7.17 s (H-8), 7.20 s (H-5), and 7.72 br s (H-4); *m/e* 380 (M^+). Integration of the nmr spectrum of the crude lactone mixture indicated the 3-carboxylic acid lactone:2-carboxylic acid lactone ratio of *ca.* 9:1.

Action of Silver Carbonate–Celite on 2,3-Bishydroxymethyl-6,7-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)naphthalene (IX).—The silver carbonate–Celite reagent (7 g) was added to a solution of the diol (383 mg) in benzene (150 ml) and the mixture was heated under reflux for 4 hr after removal of a small volume of solvent by distillation. It was then filtered and washed with chloroform, and the combined filtrate and washings were evaporated. The residual solid (308 mg, mp 257–265°) was crystallized three times from chloroform to give analytically pure 6,7-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)-2-hydroxymethylnaphthalene-3-carboxylic acid lactone (VII) (justicidin E) as needles (90 mg): mp 271–272° (lit. mp 264°,[14] 265–271°[17]); λ 5.69 μ (lactone); λ (methanol) 212 nm (ϵ 44,100), 223 (28,700), 249 (49,300), 256 (50,800), 299 sh (12,500), 313 (14,000), and 346 sh (5200); δ 5.17 s (lactone methylene), 6.07 s (two methylenedioxy groups), 6.77 m (H-6′, J = 8, 1 Hz), 6.82 (H-2′), 6.98 d (H-5′, J = 8 Hz), 7.10 s (H-8), 7.30 s (H-5), and 8.28 s (H-4); *m/e* 348 (M^+).

Anal. Calcd for $C_{20}H_{12}O_6$: C, 68.96; H, 3.47. Found: C, 68.51; H, 3.40.

The crystallization mother liquors from several such experiments were combined and subjected to preparative thin layer chromatography [1-mm silica gel PF, 20 × 20 cm developed with 1:1 petroleum ether (bp 38–60°)–ethyl acetate with trace of acetic anhydride]. The front running zone (dark blue on ultraviolet irradiation) was mainly justicidin E and the broad slower running zone (light blue on irradiation) was a mixture, eluted from the plates with ethyl acetate and crystallized from chloroform. In this way, the mixture (123 mg) yielded 23.5 mg of 6,7-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid lactone (taiwanin C) (VI) as a microcrystalline powder: mp 272–276.5° (lit. mp 275°,[14] mp 276°[16]); λ 5.67 μ (lactone); λ (methanol) 218 nm (ϵ 17,700), 222 (18,000), 252 sh (36,100), 258 (38,500), 295 (8400), 304 (8100) and 350 (4300); δ 5.37 br s (lactone methylene), 6.07 s (two methylenedioxy groups), 6.78 m (H-6′, J = 8, 1 Hz), 6.83 (H-2′), 6.98 d (H-5′, J = 8 Hz), 7.13 (H-8), 7.20 (H-5), and 7.69 br s (H-4); *m/e* 348 (M^+).

Inspection of the nmr spectrum of the crude oxidation mixture indicated the lactones were present in an approximate ratio of justicidin E (80%)–taiwanin C (20%).

Registry No.—I, 6258-38-4; II, 6258-39-5; IV, 25936-93-0; V, 31337-51-6; VI, 14944-34-4; VII, 27792-97-8.

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Notes

Lignan Lactones. Synthesis of (≡)-Collinusin and Justicidin B[1]

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There has been considerable activity recently concerning the isolation, structure elucidation, and synthesis of lignan lactones. At least 14 members[2-18] of this group of natural products have known constitutions based on 2, 3-dimethylnaphthalene. In addition, three further natural products,[19-22] which are based on a phenyldihydronaphthalene parent, have recently been described. We report here a synthesis of (≡)-collinusin (I) and justicidin B (II), a representative of each class.

Cleistanthus collinus (Roxb.) Benth. & Hook is a highly poisonous plant which has reputedly been used for insecticidal, piscicidal, and suicidal purposes.[23] From the leaves, Govindachari and coworkers isolated ellagic acid, diphyllin, and two new lactones which were named cleistanthin (a glycoside of diphyllin) and collinusin for which the structure I was proposed.[19,24] The synthesis of this lactone which we have undertaken is in complete support of this structure. The route we have utilized is based on the procedure developed by Klemm and his coworkers for a general synthesis of lignan lactones and demonstrated specifically for γ-apopicropodophyllin and dehydro-β-peltatin methyl ether.[25-27] It appeared that this pathway would be readily adaptable to collinusin; the key step (V → I), however, involving the cyclization of a cinnamyl phenylpropiolate ester to a phenyl dihydronaphthalene lactone was not entirely satisfactory, and the derived product I could only be separated from the reaction mixture with considerable difficulty and loss. The lack of specificity in cyclization may limit the general applicability of this pathway.

The key intermediate was 3, 4-dimethoxycinnamyl 3, 4-methylenedioxyphenylpropiolate (V), conveniently obtained by heating 3,4-methylenedioxyphenylpropiolic acid chloride (III) with 3,4-dimethoxycinnamyl alcohol (IV, R = H). Since the crude ester had infrared and nuclear magnetic resonance spectra in complete accord with structure V, it was used without further purification and heated under reflux with acetic anhydride to effect cyclization. Thin layer chromatographic examination of the product indicated the presence of three principal constituents, of which the fastest running, readily separable from the other two, was identified by comparison with an authentic specimen as 3,4-dimethoxycinnamyl acetate (IV, R = CH_3CO).

Satisfactory separation of the two other components was only achieved by a repetition of the thin layer chromatographic separation and recrystallization. The slower running compound (obtained pure in 9% yield) had constants in accord with the proposed structure, 3,4-dihydro-6,7-dimethoxy-3-hydroxymethyl-1-(3′,4′-methylenedioxyphenyl)naphthalene-2-carboxylic acid lactone (I). A direct comparison of the nmr spectra of this synthetic product and natural collinusin confirmed the structure.[28]

(1) (a) The awards of a research grant (AM 13708) from the National Institute of Arthritis and Metabolic Diseases, and Institutional Grant (IN-29) from the American Cancer Society and a Fellowship (to E. B.) from the Gillette Co., are gratefully acknowledged. (b) A preliminary communication outlining this work has appeared: E. Block and R. Stevenson, *Chem. Ind. (London)*, 894 (1970).

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