5.05 (d, 1, $J_{2',3'}$ = 6 Hz, C_2·H), 5.23 (dd, 1, $J_{3',4'}$ = 4 Hz, C_3·H), 5.58 (s, 1, C_1·H), 5.73 (d, 1, $J_{5,6}$ = 8 Hz, C_5H), 6.37 (d, 1, C_4·H), 7.18 (d, 1, C_6H), 9.83 (br s, 1, NH).

Anal. Calcd for $C_{13}H_{16}N_2O_7$ (312.29): C, 50.00; H, 5.17; N, 8.97. Found: C, 50.00; H, 5.30; N, 8.73.

Evaporation of the second fraction left a syrup that was crystallized from AcOEt–benzene, giving 0.09 g (4%) of 1-[4-(*R*)-acetoxy-2,3-*O*-isopropylidene-β-D-erythrofuranosyl]uracil (**10**): mp 137–138 °C; λ_{max} (MeOH) 258 nm (ε 10 700); NMR ($CDCl_3$, 60 MHz) 1.35 and 1.53 (s, 3, CMe_2), 2.07 (s, 3, OAc), 4.84 (d, 1, $J_{2',3'}$ = 6 Hz, C_2·H), 5.13 (d, 1, C_3·H), 5.72 (d, 1, $J_{5,6}$ = 8 Hz, C_5H), 5.92 (s, 1, C_1·H), 6.29 (s, 1, C_4·H), 7.27 (d, 1, C_6H), 9.25 (br s, 1, NH).

Anal. Calcd for $C_{13}H_{16}N_2O_7$ (312.29): C, 50.00; H, 5.17; N, 8.97. Found: C, 49.87; H, 5.23; N, 8.93.

Methanolysis of 8. A solution of **8** (50 mg) in MeOH (2 mL) was heated under reflux for 6 h. Evaporation of the solvent in vacuo gave a crystalline solid which was shown by NMR to consist of **4** and **5** in a ratio of 1:2.

Acetolysis of 8. A solution of **8** (300 mg) in AcOH (2 mL) was stored at room temperature for 2 h. The solvent was removed in vacuo, and the residue was coevaporated several times with AcOEt, giving a syrup which was shown by NMR to consist of **9** and **10** in a ratio of 1:1.

N^6,N^6-Dibenzoyl-2′,3′-*O*-isopropylideneadenosine-5′-carboxylic acid (**11a**) was prepared from 2′,3′-*O*-isopropylideneadenosine-5′-carboxylic acid[15] by condensation with benzyl alcohol, using *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline, followed by N^6,N^6-dibenzoylation with benzoyl chloride in pyridine and catalytic hydrogenation of the benzyl group in the presence of Pearlman catalyst[16] in AcOEt. The crude product was purified by crystallization from 1,2-dimethoxyethane to give the acid **11a** as the solvate: mp 119–120 °C dec; λ_{max} (MeOH) 251 nm (ε 39 400) 278 (sh, 31 100); NMR ($CDCl_3$, 60 MHz) δ 1.38 and 1.59 (s, 3, CMe_2), 3.39 (s, 6, MeO's), 3.54 (s, 4, OCH_2CH_2O), 4.75 (s, 1, C_4·H), 5.37 (s, 2, C_2·H, C_3·H), 6.29 (s, 1, C_1·H), 7.2–8.0 (m, 10, ArH), 8.48 (s, 1, C_2H or C_8H), 8.52 (s, 1, C_2H or C_8H), 10.25 (br s, 1, CO_2H).

Anal. Calcd for $C_{27}H_{23}N_5O_7 \cdot C_4H_{10}O_2$ (619.64): C, 60.09; H, 5.37; N, 11.30. Found: C, 60.01; H, 5.54; N, 11.27. The overall yield was 53%.

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Registry No. 1, 71774-76-0; 4, 71774-77-1; 5, 71806-80-9; 6 isomer A, 71774-78-2; 6 isomer B, 71806-81-0; 7, 71774-79-3; 8, 71774-80-6; 9, 71774-81-7; 10, 71806-82-1; 11a, 71774-83-9; uridine-5′-carboxylic acid, 3415-07-4; 2,2-dimethoxyethane, 534-15-6; *p*-toluenesulfonylhydrazine, 1576-35-8; 2′,3′-*O*-isopropylideneadenosine-5′-carboxylic acid, 3415-09-6.

(15) Harmon, R. E.; Zenarosa, C. V.; Gupta, S. K. *Chem. Ind.* **1969**, 1141.

(16) Hiskey, R. G.; Northrop, R. C. *J. Am. Chem. Soc.* **1961**, *83*, 4798.

Simple Synthetic Route to Lasiodiplodin

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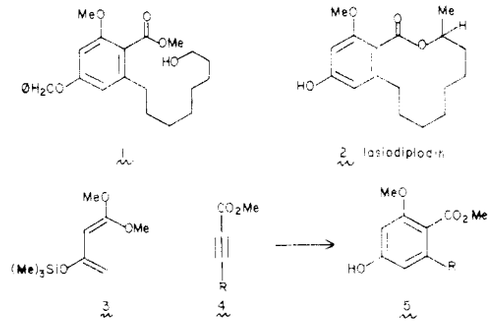
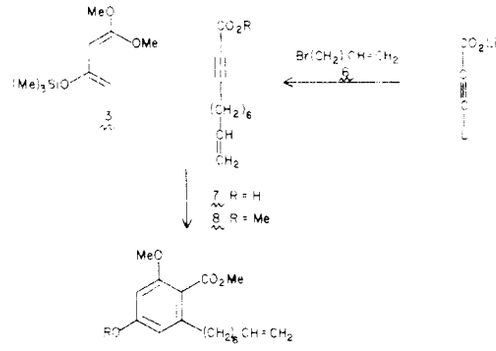
Recently Gerlach and Thalmann described the total synthesis of the plant growth inhibitor lasiodiplodin (**2**).[1,2] Gerlach's synthesis passed through the tetrasubstituted aromatic system **1**. The yields in going from **1** to **2** were excellent.

In examining the structure of lasiodiplodin and its precursor, **1**, we took note of the presence of a monomethylated resorcinol derivative wherein the methoxy group is ortho to a carbonyl function. Recently, we described a rather direct construction of such a ring system.[3] Our approach is summarized in the formalism **3** + **4** → **5**.



We had only investigated this reaction in the two cases where R was hydrogen or carbomethoxyl. It was thus of interest to explore the feasibility of a direct synthesis of a tetrasubstituted benzenoid product such as **5**, where R would be alkyl. We describe our findings with respect to applying this methodology to a synthesis of lasiodiplodin. Specifically, we focused on a synthesis of compound **1**.

The required dienophile, **7**, was easily obtained by drawing upon the chemistry of Carlson.[4] Thus, alkylation of the dianion of propiolic acid with the commercially available 1-bromo-7-octene (**6**) followed by suitable workup



afforded a 68% yield of crude acid **7**. This was converted (potassium carbonate, methyl iodide, dimethyl formamide) into **8**, which was readily purified by distillation. The yield of pure **8** over the two steps was 55%.

Compound **8** was heated with **3** in xylene at ca. 140 °C for 18 h. Workup in the usual way afforded crude **9**. To merge most conveniently with the Gerlach's synthesis, we benzylated **9**. The overall yield of the resultant **10** over the two steps was 35%. Hydroboration–oxidation of **10** afforded an 80% yield of **1**. Its structure followed from its spectral properties and from the correspondence of these properties with those described by Gerlach.[1]

The yield of the Diels–Alder step was thus, not surprisingly, lower than those encountered in the two model cases described above. Nonetheless, it is seen that this methodology provides rapid access to tetrasubstituted

(1) H. Gerlach and A. Thalmann, *Helv. Chim. Acta*, **60**, 2866 (1977).

(2) A recent study in this series was provided by T. Takahashi, K. Kasuga, and J. Tsuji, *Tetrahedron Lett.*, 4917 (1978). Though the route is commendably brief, in its published form it does not provide differentiation among the aromatic oxygen functions.

(3) S. Danishefsky, R. K. Singh, and R. B. Gammill, *J. Org. Chem.*, **43**, 379 (1978).

(4) R. M. Carlson, A. R. Oyler, and J. C. Peterson, *J. Org. Chem.*, **40**, 1610 (1975).

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aromatic systems with differentiated oxygens. From this perspective it is likely to be of value in other synthetic enterprises.

Experimental Section[5]

Methyl Undec-2-yn-10-enoate (8). To a solution of 5.65 g (0.0559 mol) diisopropylamine in 20 mL of dry tetrahydrofuran under N_2 and at −78 °C, was added 34.9 mL of a 1.6 M solution of *n*-butyllithium in hexane (0.0559 mol) in a rapid dropwise fashion. The resulting solution was stirred for 45 min at −41 °C. To this solution at −41 °C were added 1.92 g (0.0275 mol) of propiolic acid and then 20 mL of dry hexamethylphosphoramide. This mixture was warmed to −15 °C and stirred for 2 h. A 5.2-g (0.0272-mol) sample of 1-bromo-7-octene (Chemical Samples) was then added dropwise over ca. 10 min. The reaction mixture was then allowed to warm to room temperature and stirred for 18 h.

The reaction mixture was poured into 400 mL of water and extracted (4 × 200 mL) with CH_2Cl_2. The aqueous layer was acidified to pH 1 with 1 N HCl, and the product was extracted (3 × 150 mL) with ether. The combined ether extracts were washed with water and with brine, dried ($MgSO_4$), and freed of solvent to afford 3.33 g (68%) of crude acid **7**: $\bar{\nu}$ ($CHCl_3$) 3600–3000 (br), 2240, 1685 cm^{-1}.

A mixture of 3.17 g of crude acid (2.50 g, 0.0181 mol) of anhydrous potassium carbonate and 6 mL of methyl iodide in 38 mL of dry dimethylformamide was stirred overnight under nitrogen at room temperature. It was poured into 400 mL of water and 350 mL of ether. The organic layer was washed (2 × 150 mL) with water and with brine, dried ($MgSO_4$), and freed of solvent to afford 3.06 g (90%) of the crude ester. Kugelrohr distillation, 65–75 °C (0.25 mm), afforded 2.82 g of the ester **8** as a colorless liquid: $\bar{\nu}$ ($CHCl_3$) 2230, 1715 cm^{-1}; δ ($CDCl_3$) 6.1–5.3 (m, 1 H), 5.03 (br d), 4.78 (br s, 2 H), 3.71 (s, 3 H), 1.0–2.50 (m, 12 H).

Methyl 2-Methoxy-4-(benzyloxy)-6-(oct-7-en-1-yl)benzoate (10). A solution of 0.848 g (0.0044 mol) of **8** and 2.65 g (0.0131 mol) of diene **3** in 2 mL of dry xylene was heated under nitrogen at 141 °C for 18 h. Upon the solution cooled, the solvent was removed in vacuo, and the residue was taken up in 10 mL of tetrahydrofuran and 10 mL of 0.1 N HCl. This mixture was stirred for 1.5 h at room temperature and was poured into 200 mL of ether and 100 mL of H_2O. The organic layer was washed with 1 N HCl (2 × 100 mL) and with brine. It was dried ($MgSO_4$), freed of solvent in vacuo, taken up in 3:1 hexane:ethyl acetate, and filtered through 10 g of Florisil. Concentration afforded 1.33 g of crude **9** which was submitted to the next step.

To a slurry under N_2 of 0.0068 mol of NaH (0.330 g of a 50% emulsion washed with pentane) in 15 mL of dry tetrahydrofuran was added a solution of 1.25 g of crude **9** in 10 mL of tetrahydrofuran at such a rate that the evolution of gas was controlled. After the mixture was stirred for ca. 10 min at room temperature, 3 mL of benzyl chloride followed by 0.800 g (0.001 mol) of sodium iodide was added. This reaction mixture was heated for 16 h under reflux, cooled to room temperature, and poured into 250 mL of water layered with 200 mL of ether. The organic layer when washed with H_2O and with brine, dried ($MgSO_4$), and freed of solvent afforded an oil which, after chromatography on silica gel and elution with 6:1 hexane:ethyl acetate, afforded 0.580 g (35%) of **10** as an oil: δ ($CDCl_3$) 7.38 (br s, 5 H), 6.41 (s, 2 H), 6.18–5.35 (m, 1 H), 5.05 (m and s, 3 H), 4.82 (br s, 1 H), 3.87 (s, 3 H), 3.75 (s, 3 H), 2.72–2.33 (m, 2 H), 2.26–1.83 (m, 2 H), 1.83–0.9 (m, 8 H); the spectrum also included a small signal at δ 7.2–6.8 which arises from an unknown trace impurity; mass spectrum, *m/e* calcd for $C_{24}H_{30}O_4$ 382.2144, found, 382.2119.

Methyl 2-Methoxy-4-(benzyloxy)-6-(8-hydroxyoctyl)-benzoate (1). To a solution of 0.058 g (0.00152 mol) of **10** in 30 mL of dry tetrahydrofuran under nitrogen and at 0 °C was added 2.9 mL of 1.0 M diborane/tetrahydrofuran (0.0029 mol) in a rapid dropwise fashion. The reaction mixture was allowed to warm to room temperature and to stir for 30 min. It was then cooled to 0 °C, and excess diborane was destroyed by the dropwise addition of water. Oxidation was accomplished by addition of 1.3 mL of 10% sodium hydroxide and 1.3 mL of 30% hydrogen peroxide and heating at 50 °C for 30 min.

The reaction mixture was poured into 300 mL of dilute hydrochloric acid and 300 mL of ether. The organic layer was washed with 100 mL of water and brine, dried, and freed of solvent to afford 0.585 g of a crude oil. Chromatography on silica gel using 1:1 hexane:ethyl acetate afforded 0.485 g (80%) of pure hydroxy ester **1** as a colorless oil: NMR and IR spectra were identical with those reported by Gerlach; mass spectrum, *m/e* calcd for $C_{24}H_{32}O_5$ 400.2250 (P), found 400.2249 (P).

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Registry No. **1**, 65716-56-5; **3**, 61539-61-5; **6**, 2695-48-9; **7**, 71819-27-7; **8**, 71819-28-8; **9**, 71838-34-1; **10**, 71819-29-9; propiolic acid, 471-25-0.

(5) Boiling points are uncorrected. Infrared measurements were obtained from a Perkin-Elmer 247 recording spectrometer. NMR spectra were obtained from a Varian Associates T60-A system using tetramethylsilane as an internal standard. Chemical shifts are given in parts per million from Me_4Si (δ). Low-resolution mass spectra were obtained from an LKB-9000 unit by direct insertion. High-resolution mass spectra were obtained from a Varian Associates CH-5 system.

Sulfonamidyls. 3.[1] Electron Spin Resonance Spectroscopic Study of New Acyclic and Cyclic Sulfonamidyl Radicals

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In two earlier communications[1] we have reported electron spin resonance (ESR) spectral data for *N*-alkylsulfonamidyl[1a] ($R_1SO_2\dot{N}R_2$) and *N*-alkoxysulfonamidyl radicals[1b] ($R_1SO_2\dot{N}OR_2$).[2] In a subsequent Japanese paper[3] ESR spectra were described for some *N*-arylsulfonamidyl radicals and, very recently, ESR data for an additional *N*-alkoxysulfonamidyl were reported by Forrester et al.[4] We have proposed[1] that sulfonamidyls reside in a π-electronic ground state, but noted some interesting differences between the ESR spectral features of sulfonamidyls and the corresponding carboxamidyls ($R_1C\dot{O}NR_2$), reported previously.[5,6]

In this note we present new ESR data which shed further light upon the structure of sulfonamidyl radicals. In all cases these rather short-lived radicals were produced by photolysis of the corresponding *N*-bromosulfonamides directly in the cavity of the ESR spectrometer at low temperatures. Alternatively, two *N*-alkoxysulfonamidyls were also generated by hydrogen abstraction from the parent sulfonamide by *tert*-butoxyl radicals, obtained from thermolysis of di-*tert*-butyl peroxyoxalate (DBPO).

$$\underset{\text{Y = alkyl, alkoxy}}{\overset{\displaystyle Br}{\overset{|}{RSO_2NY}}} \xrightarrow{h\nu} RSO_2\dot{N}Y \xleftarrow{t\text{-BuO}\cdot} \underset{\text{Y = alkoxy}}{\overset{\displaystyle H}{\overset{|}{RSO_2NY}}}$$

In order to examine the possibility that the smaller nitrogen hyperfine splitting constants (hfc's) of acyclic

(1) (a) Part 1: G. Zomer and J. B. F. N. Engberts, *Tetrahedron Lett.*, 3901 (1977); (b) Part 2: H. Teeninga and J. B. F. N. Engberts, *Recl. Trav. Chim. Pays-Bas*, **97**, 59 (1978).

(2) After our communications we were informed by Dr. R. W. Gellert that ESR spectral properties of several sulfonamidyls have been described in his M.S. thesis, Kansas State University, 1973. However, to the best of our knowledge, this work has not been published.

(3) Y. Miura, Y. Nakamura, and M. Kinoshita, *Bull. Chem. Soc. Jpn.* **51**, 947 (1978).

(4) A. R. Forrester, E. M. Johansson, and R. H. Thomson, *J. Chem. Soc, Perkin Trans. 1*, 1112 (1979).

(5) W. C. Danen and R. W. Gellert, *J. Am. Chem. Soc.*, **94**, 6853 (1972).

(6) T. Koenig, J. A. Hoobler, and W. R. Mabey, *J. Am. Chem. Soc.*, **94**, 2514 (1972).

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