(br, 2 H), 1.59 (band, 8 H), 3.93 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 24.0, 25.2, 35.2, 64.1, 109.0.

IV. 1,4-Dioxospiro[4.4]nonane. This compound was prepared in the same manner as in III above: bp 68–71 °C (28 Torr); ^1H NMR ($CDCl_3$) δ 1.68 (band, 4 H), 1.77 (band, 4 H), 3.90 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 23.6, 35.9, 64.2, 118.5.

General Procedure for the Preparation of Cyclic Ethers by Transacetalization Reactions. Cyclic ethers were prepared by allowing ketals **1–5** to react with the appropriate alcohols in the presence of titanium tetrachloride as described below.

A 250-mL three-neck round-bottom flask was equipped with a gas inlet, a 25-mL addition funnel, and a septum. The system was purged with dry nitrogen after which methylene chloride (7 mL/mmol ROH) distilled from phosphorus pentoxide was added to the reaction flask, and 0.7 mL CH_2Cl_2/mmol $TiCl_4$ was added to the addition funnel. The flask was cooled to the appropriate temperature (0 or −45 °C). Weighed quantities of alcohol (10–20 mmol) and ketal (20–40 mmol) were added to the flask via syringe through the septum. Titanium tetrachloride (20–40 mmol) was added to the addition funnel. After thermal equilibrium the acid solution was added dropwise. (For cyclizations run at room temperature the titanium tetrachloride was added at 0 °C.) Reactions were run for ca. 1–4 h under nitrogen. Upon completion, reactions were quenched with 10 mL of methanol followed by 50 mL of 1 N hydrochloric acid saturated with sodium chloride. After coming to the ambient temperature, the organic layer was separated, and the aqueous phase was extracted with ether. The organic layers were combined and dried over magnesium sulfate, and the products were concentrated at the aspirator. Samples were isolated for analysis by preparative GLC or Kugelrohr distillation.

Characterization. Gas chromatographic analyses were performed with Hewlett-Packard Models 5710 and 5790 instruments equipped with electronic integrators and 10 ft × $^1/_8$ in. 10% SP1000 and 25 m methyl silicone (capillary) columns, respectively. NMR spectra were taken with General Electric QE-300 and Varian FT-80A instruments.

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Registry No. **2**, 10143-67-6; **3**, 77-76-9; **4**, 177-10-6; **5**, 176-32-9; **6**, 1768-64-5; *trans*-**7**, 25999-33-1; *cis*-**7**, 25999-40-0; **8**, 92826-98-7; **9**, 119568-20-6; *E*-**10**, 119568-21-7; *Z*-**10**, 119568-22-8; **11**, 119568-23-9; **12**, 53045-59-3; **13**, 119568-24-0; **14**, 119568-25-1; **15**, 119568-26-2; **16**, 119568-27-3; 4-phenyl-3-butyn-1-ol, 10229-11-5; 3-buten-1-ol, 627-27-0; *trans*-3-hexen-1-ol, 928-97-2; 4-penten-2-ol, 625-31-0; 3-butyn-1-ol, 927-74-2; bis(2-methoxyethoxy)methane, 4431-83-8; MEM chloride, 3970-21-6; 2-methoxyethanol, 109-86-4; acetaldehyde, 75-07-0; 1-(2-methoxyethoxy)-1-chloroethane, 119593-85-0.

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A New Route to Annelated Dihydrofurofurans. Synthesis of 6,8-Dideoxyversicolorin A

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The highly toxic fungal metabolite aflatoxin B_1 (**1**), and its carcinogenic biosynthetic precursor versicolorin A (**2**), are both annelated derivatives of 3a,6a-dihydro[2,3-*b*]-furofuran (**3**).[1]

A number of procedures have been described for the construction of the reduced furofuran skeleton.[2] The introduction of unsaturation into this system to give the enol ether functionality has generally been accomplished under vigorous pyrolysis conditions.[2a,e,f] We now report a new short and efficient protocol for the construction of an unsaturated furofuran based upon a key phenolic Claisen rearrangement step, as well as a mild selenoxide elimination for the generation of the cyclic enol ether function. The utility of this approach is illustrated by a synthesis of 6,8-dideoxyversicolorin A (**4**) from 1,3-dihydroxyanthraquinone (**5**).[3]

The required aliphatic reagent for this synthesis was 2,5-hexadien-1-ol (**6**). An inconvenient preparation of this alcohol has been reported.[4] We have found that it may be readily prepared by a two-step process with inexpensive precursors as starting materials. Thus, the coupling of allyl bromide with propargyl alcohol gave 5-hexen-2-yn-1-ol,[5] which was converted to **6** by reduction with lithium aluminum hydride.

1,3-Dihydroxyanthraquinone (**5**) was converted selectively into its 3-MOM ether (**7**) by reaction with methoxymethyl chloride and *N,N*-diisopropylethylamine. Mitsunobu condensation[6] of **7** with alcohol **6** afforded the corresponding ether **8** in 82% yield. The reductive Claisen rearrangement of **8** in aqueous DMF[7] proceeded smoothly to give the 2-dienylanthraquinone **9** (86%), which was deblocked by methanolic HCl to give the phenol **10** (78%). Oxidative cleavage of **10** by OsO_4–$NaIO_4$ directly furnished the lactol **12** (74%) through the spontaneous intramolecular cyclization of the intermediary dialdehyde **11**. Attempted conversion of lactol **12** to an α-phenylseleno ether with *N*-(phenylseleno)phthalimide[8] failed. However, treatment of **12** with benzeneselenol in refluxing benzene[9] gave the desired selenide **13** (81%) as a separable 3:2 isomer mixture. Either isomer readily underwent oxidative selenide elimination on treatment with hydrogen peroxide to 6,8-dideoxyversicolorin A (**4**) in 70% yield.

With an appropriately blocked 1,3,6,8-tetrahydroxyanthraquinone as starting material, the same methodology should be applicable to the synthesis of versicolorin A itself.

Experimental Section

General. All melting points are uncorrected. All NMR spectra were done in $CDCl_3$ solution. Elemental analyses (C, H, N, S) were carried out by Atlantic Microlabs, Atlanta, GA. Selenium analyses were done by Galbraith labs, Knoxville, TN.

2,5-Hexadien-1-ol (6). To a suspension of LAH (5.4 g, 0.14 mol) in THF (250 mL) was added dropwise a solution of 5-hex-

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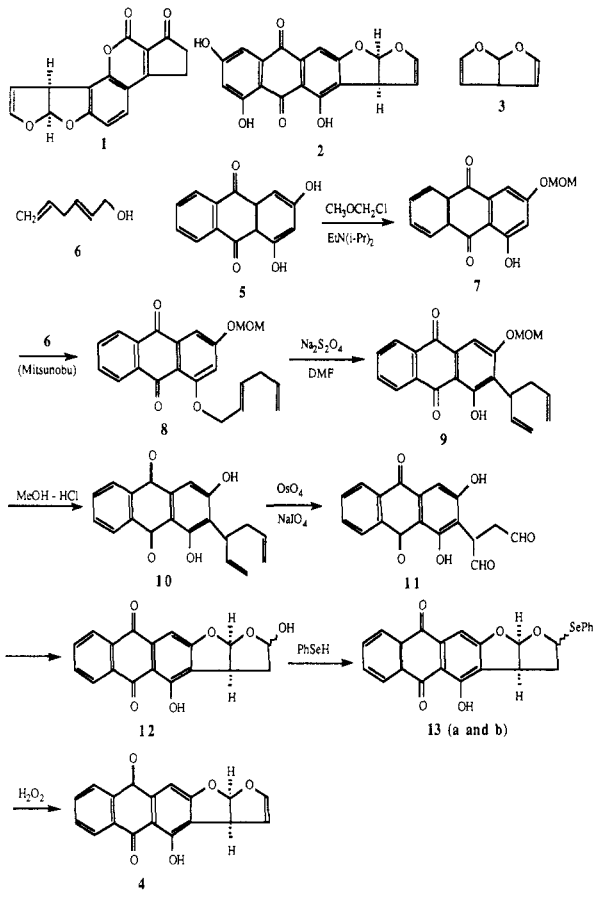

en-2-yn-1-ol[5] (10.6 g, 0.11 mol) in THF (250 mL). After the addition was complete, the mixture was refluxed for 3 h and cooled, and ice water (20 mL) was added dropwise while cooling in ice. After filtration, the solvent was removed and the residue was extracted with ether. The ether layer was dried and concentrated, and the residue was distilled to give 2,5-hexadien-1-ol (8) (9.7 g, 0.1 mol, 90%) as colorless liquid (bp 73–75 °C/20 mm): NMR δ 1.96 (s, 1 H), 2.80 (m, 2 H), 4.07 (m, 2 H), 4.07 (m, 2 H), 4.95–5.12 (m, 2 H), 5.64–5.74 (m, 3 H).

1-Hydroxy-3-(methoxymethoxy)anthraquinone (7). To a stirred suspension of 1,3-dihydroxyanthraquinone[3] (10 g, 42 mmol) and chloromethyl methyl ether (3.67 g, 46 mmol) in dry THF (200 mL) was added diisopropylethylamine (8.19 g, 63 mmol) dropwise at room temperature. After 1 h, the reaction mixture was poured into water. The solid was collected, washed with water, and dried. The crude product was chromatographed on silica, with methylene chloride as eluent, to afford compound **7** as a bright yellow solid (11.83 g, 95%), which was recrystallized from ethanol–methylene chloride to give yellow crystals, mp 130–132 °C; NMR δ 3.51 (s, 3 H), 5.29 (s, 2 H), 6.88 (d, 1 H, J = 2.4 Hz), 7.45 (d, 1 H, J = 2.4 Hz), 7.77–7.81 (m, 2 H), 8.22–8.31 (m, 2 H), 12.81 (s, 1 H); MS 284 (M^+, 100), 254 (13), 139 (13), 127 (10), 77 (10). Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.26. Found: C, 67.81; H, 4.21.

3-(Methoxymethoxy)-1-(2,5-hexadien-1-yloxy)anthraquinone (8). To a stirred solution of **7** (10 g, 35.2 mmol), triphenyl phosphine (11.24 g, 42.9 mmol), and 2,5-hexadien-1-ol (**6**) (5.2 mL, 52.3 mmol) in dry THF (300 mL) at 0 °C was added dropwise diethyl azodicarboxylate (9 mL, 56.3 mmol) in dry THF (50 mL). The mixture was then stirred at room temperature for 3 h. The solvent was removed under reduced pressure to give a red syrup, which was filtered through neutral alumina with CH_2Cl_2 and then chromatographed (silica gel, 3:1, hexane–ethyl acetate) to give, after crystallization from ethanol, **8** (10.5 g, 28.8 mmol, 82%) as greenish yellow crystals: mp 103–104 °C; NMR δ 2.87–2.93 (m, 2 H), 3.52 (s, 3 H), 4.71–4.73 (d, 1 H, J = 5.0 Hz), 5.03–5.13 (m, 2 H), 5.32 (s, 2 H), 5.78–6.10 (m, 2 H), 6.95 (d, 2 H, J = 2.4 Hz), 7.59 (d, 1 H, J = 2.3 Hz), 7.69–7.82 (m, 2 H), 8.19–8.38 (m, 3 H); MS 364 (M^+, 3.5), 323 (7.7), 293 (20.8), 284 (49.5), 254 (14.7), 211 (5.5), 167 (6.2), 139 (15.5), 79 (15.8), 45 (100). Anal. Calcd for $C_{22}H_{20}O_5$: C, 72.53; H, 5.49. Found: C, 72.31; H, 5.59.

1-Hydroxy-2-(1,5-hexadien-3-yl)-3-(methoxymethoxy)anthraquinone (9). To a stirred solution of **8** (8 g, 22.0 mmol), in DMF (160 mL) and water (160 mL) under N_2, was added sodium dithionite (4.38 g, 30.8 mmol). The reaction mixture was heated at 70 °C for 1 h and then cooled to room temperature. Air was bubbled in for 1 h, and the mixture was diluted with CH_2Cl_2 (500 mL). The organic phase was separated and washed repeatedly with water, the solvent was removed, and the residue was crystallized from CH_2Cl_2·MeOH to give **9** (6.88 g, 18.9 mmol, 86%) as light yellow crystals: mp 111–112 °C; NMR 2.63–2.79 (m, 2 H), 3.52 (s, 3 H), 4.18–4.30 (m, 1 H), 4.89–5.15 (m, 4 H), 5.39 (s, 2 H), 5.64–5.85 (m, 1 H), 6.26–6.40 (m, 1 H), 7.55 (s, 1 H), 7.72–7.82 (m, 2 H), 8.23–8.38 (m, 2 H), 13.27 (s, 1 H); MS 364 (M^+, 1.2), 323 (64.1), 291 (13.2), 277 (45.4), 253 (5.7), 221 (5), 165 (13.5), 151 (5.8), 45 (100). Anal. Calcd for $C_{22}H_{20}O_5$: C, 72.53; H, 5.49. Found: C, 72.39; H, 5.55.

1,3-Dihydroxy-2-(1,5-hexadien-3-yl)anthraquinone (10). A mixture of **9** (6.0 g, 16.48 mmol), MeOH (240 mL), and concentrated HCl (12 mL) was refluxed for 30 min and cooled, and the MeOH was removed. The residue was taken up in CH_2Cl_2 (250 mL), and the organic layer was washed with water, dried, and evaporated. The residue was crystallized from ethanol to give **10** (4.12 g, 12.9 mmol, 78%) as orange crystals: mp 225–226 °C; NMR δ 2.63–2.71 (m, 2 H), 4.24–4.35 (m, 1 H), 4.92–5.07 (m, 2 H), 5.25–5.35 (m, 2 H), 5.68–5.85 (m, 1 H), 6.24–6.41 (m, 1 H), 7.26 (s, 1 H), 7.38 (s, 1 H), 7.74–7.84 (m, 2 H), 8.24–8.33 (m, 2 H), 13.46 (s, 1 H); MS 320 (M^+, 3.4), 280 (18.9), 237 (6), 176 (5.6), 165 (5.1), 152 (5.0), 77 (5.3). Anal. Calcd for $C_{20}H_{16}O_4$: C, 75.00; H, 5.00. Found: C, 75.06; H, 5.03.

2,4-Dihydroxy-5,10-dioxo-2,3,3a,12a-tetrahydroanthra[2,3-*b*]furo[2,3-*d*]furan (12). To a solution of **10** (5 g, 15.6 mmol) in THF (200 mL) and water (60 mL) was added $NaIO_4$ (20 g, 93.5 mmol) followed by 10 mL (0.0016 mmol) of 4% aqueous OsO_4 at 0 °C. The mixture was stirred for 6 h, the solid was filtered, and the residue, obtained after removal of the solvent, was taken up in ethyl acetate (250 mL). The solvent was washed with water (5 × 50 mL), dried, and evaporated. The chromatographed residue (silica gel, 2:1 hexane–ethyl acetate), after crystallization from benzene, gave **12** (3.75 g, 11.5 mmol, 75%) as light yellow crystals: mp 218–220 °C dec; NMR δ 2.56–2.62 (m, 2 H), 4.12–4.20 (m, 1 H), 5.77–5.80 (m, 1 H), 6.54 (d, 1 H, J = 6.2 Hz), 7.32–7.47 (m, 1 H), 7.76–7.83 (m, 2 H), 8.24–8.32 (m, 2 H), 13.01 (s, 1 H); MS 324 (M^+, 18.8), 296 (61.4), 278 (64.2), 277 (84.1), 268 (80.5), 267 (100), 253 (66.2), 165 (35.7), 139 (25.8), 77 (19.2). Anal. Calcd for $C_{18}H_{12}O_6$: C, 66.67; H, 3.70. Found: C, 66.06; H, 3.75.

2-(Phenylseleno)-4-hydroxy-5,10-dioxo-2,3,3a,12a-tetrahydroanthra[2,3-*b*]furo[3,2-*d*]furan (13). To a solution of diphenyl diselenide (1.45 g, 4.65 mmol) in THF (10 mL) was added 50% aqueous hypophosphorous acid (3.8 mL). The mixture was refluxed for 30 min and then cooled. The resulting benzeneselenol was extracted into benzene (200 mL), **12** (2.0 g, 6.2 mmol) and few crystals of *p*-toluenesulfonic acid were added, and the mixture was refluxed for 3 h. The cooled solution was washed with water, 5% aqueous $NaHCO_3$, and water. The dried solvent was removed, and the residue was chromatographed over silica (3:1 hexane–ethyl acetate) to give isomers **13a** (0.686 g, 3.0 mmol) and **13b** (0.457 g, 2.0 mmol) as light yellow solids (81% overall yield), both of which crystallized from CH_2Cl_2·MeOH.

Data for **13a**: mp 207–209 °C; NMR δ 2.18–2.45 (m, 1 H), 2.74–2.83 (m, 1 H), 4.10–4.17 (m, 1 H), 5.42–5.50 (m, 1 H), 6.52 (d, 1 H, J = 5.9 Hz), 7.24–7.32 (m, 5 H), 7.62–7.83 (m, 3 H), 8.23–8.30 (m, 2 H), 13.01 (s, 1 H); MS 464 (M^+ + 1, 0.5), 462 (0.3), 314 (0.9), 308 (18.4), 307 (100), 278 (34.2), 249 (5.7), 165 (17.1), 158 (12.5), 152 (8.8), 139 (8), 105 (6.8), 77 (16.9). Anal. Calcd for $C_{24}H_{16}O_5Se$: C, 62.20; H, 3.46. Found: C, 62.06; H, 3.51.

Data for **13b**: mp 170–172 °C; NMR δ 2.74–2.90 (m, 2 H), 4.26–4.30 (m, 1 H), 6.02 (m, 1 H), 6.57 (d, 1 H, J = 6.1 Hz), 7.25–7.39 (m, 5 H), 7.52–7.84 (m, 3 H), 8.23–8.33 (m, 2 H), 13.08 (s, 1 H); MS 464 (M^+ + 1, 1.8), 463 (M^+, 0.3), 462 (1.0), 308 (20.6), 307 (100), 279 (29.7), 265 (8.2), 251 (4.9), 237 (4.6), 176 (2.9), 157 (5.4), 77 (8.9). Anal. Calcd for $C_{24}H_{16}O_5Se$: C, 62.20; H, 3.46. Found: C, 62.36; H, 3.53.

6,8-Dideoxyversicolorin A (4). To the solution of **13a** or **13b** (0.50 g, 1.08 mmol) in THF (10 mL) was added 30% hydrogen peroxide (1 mL) at 0 °C, and the solution was stirred for 3 h. The solvent was removed, and the residue was extracted into CH_2Cl_2

(25 mL) and washed with water (2 × 20 mL). The dried solvent was removed, and the residue was chromatographed over silica (3:1 hexane–ethyl acetate) to give, after crystallization from ethanol, **4** (0.23 g, 0.76 mmol, 70%) as yellow crystals: mp 242–245 °C dec; NMR δ 4.73–4.77 (m, 1 H), 5.45–5.48 (t, 1 H, J = 2.5 Hz), 6.50–6.52 (t, 1 H, J = 2.3 Hz), 6.84 (d, 1 H, J = 7.2 Hz), 7.74–7.84 (m, 3 H), 8.25–8.31 (m, 2 H), 12.93 (s, 1 H); MS 307 (M^+ + 1, 10.7), 306 (M^+, 47.3), 297 (46.9), 278 (67), 277 (100), 249 (13.6), 221 (9.2), 193 (7.9), 165 (28.1), 163 (13.7), 139 (16.4), 105 (8.3), 77 (10.2). Anal. Calcd for $C_{18}H_{10}O_5$: C, 70.59; H, 3.21. Found: C, 70.31; H, 3.53.

Registry No. **4**, 119998-28-6; **6**, 42185-95-5; **7**, 64517-18-6; **8**, 120022-33-5; **9**, 120022-34-6; **10**, 120022-35-7; **12** (isomer 1), 119998-26-4; **12** (isomer 2), 120056-18-0; **13** (isomer 1), 119998-27-5; **13** (isomer 2), 120056-19-1; 5-hexen-2-yn-1-ol, 2749-86-2; 13-dihydroxyanthraquinone, 518-83-2; benzeneselenol, 645-96-5.

Regiospecific Aryl Nitration of Meso-Substituted Tetraarylporphyrins: A Simple Route to Bifunctional Porphyrins

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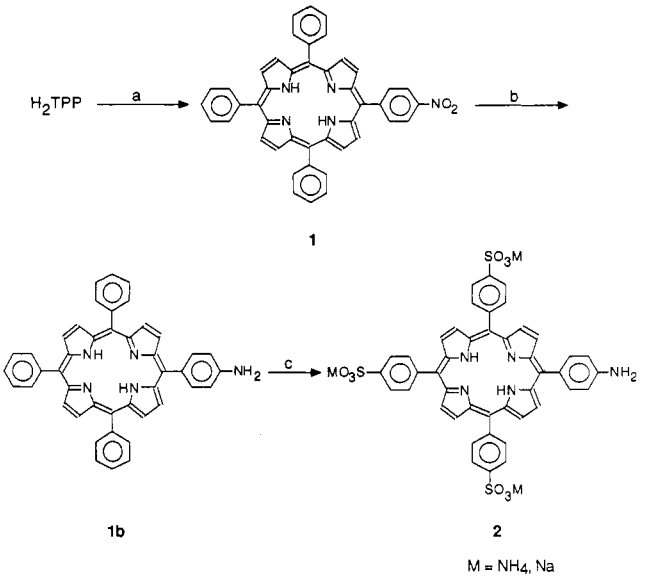
The selective localization of naturally occurring[1] and synthetic porphyrins[2] in malignant tumor tissue has been recognized for decades. Radiometalated porphyrinate derivatives have also been observed to localize in the kidney, liver, and spleen.[2c] In order to mitigate unwanted organ localization and increase tumor uptake of these derivatives, efforts have been directed at covalently attaching unsymmetrically aryl, functionalized porphyrins to tumor-selective, monoclonal antibodies.[3] The objective of this approach is to convey a stable radionuclide (metal) of diagnostic or therapeutic potential to the tumor tissue or antigen site. Unsymmetrically functionalized prophyrins have also been covalently incorporated into polymer backbones[4] as well as attached to cyclodextrins[5] and are known to serve as useful synthetic precursors to monooxygenase and allosteric enzyme model systems.[6]

All synthetic routes to unsymmetrically functionalized porphyrins such as **1a** have derived from low yield (<5%), crossed-Rothemund condensations.[3-7] Despite recent and dramatic advances in these procedures, statistical mixtures of porphyrins are obtained that are difficult and tedious to separate by preparative techniques.[8] The evolution of

Scheme I[a]

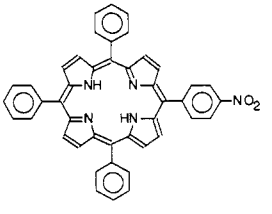


[a] (a) Fuming HNO_3 (17 equiv), $CHCl_3$, 0–5 °C (55%); (b) $SnCl_2$, concentrated HCl, 65 °C (75%); (c) concentrated H_2SO_4, 70 °C (92%).

synthetic, porphyrin enzyme mimics and radiotherapeutic agents is dependent upon access to this relatively new class of compounds.

The direct, peripheral functionalization of porphyrins using electrophiles or free radicals has been mainly restricted to modification of the macrocycle ring at either the meso or the β pyrrole carbon.[9] Electrophillic addition of sulfuric acid to the phenyl group of tetraphenylporphyrin is the only example of aryl-group modification without concomitant attack on the macrocycle ring.[10] In contrast to sulfonation, the direct nitration of metallo tetraarylporphyrinates using radical conditions has been noted to mononitrate the macrocyle at the β-position in good to excellent yields by using a variety of oxidants.[11] Both radical[12] and sulfuric acid catalyzed[13] nitrations of free-base tetraphenylporphyrin are reported to afford β and various meso substitution products. No observation of phenyl-group nitration was made in any of these studies.

In view of these limitations and our interest in developing new bifunctional chelants for our radioimmunotherapy program, we developed an attractive, alternative synthesis of mono(nitrophenyl)triphenylporphyrin (**1a**)



1a

through regiospecific aryl nitration of commercially available tetraphenylporphyrin.[14] Reduction of **1a** to the

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