[a]anthracene, 60967-88-6; 1-hydroxybenzo[a]anthracene, 69847-26-3; 2-hydroxybenzo[a]anthracene, 69847-27-4; *trans*-3,4-dihydroxy-3,4-dihydrobenzo[a]anthracene, 60967-89-7; 3-hydroxybenzo[a]-anthracene, 4834-35-9; 4-hydroxybenzo[a]anthracene, 5133-12-0; *trans*-8,9-dihydroxy-8,9-dihydrobenzo[a]anthracene, 34501-24-1; 8-hydroxybenzo[a]anthracene, 34501-23-0; 9-hydroxybenzo[a]-anthracene, 34570-62-2; *trans*-10,11-dihydroxy-10,11-dihydrobenzo-[a]anthracene, 60967-90-0; 10-hydroxybenzo[a]anthracene, 69884-53-3; 11-hydroxybenzo[a]anthracene, 63019-35-2; 8-butoxybenzo-[a]pyrene, 78673-06-0; Bu_4NOH, 2052-49-5.

Reactions of Ketene Acetals. 13.[1] Synthesis of Contiguously Trihydroxylated Naphtho- and Anthraquinones

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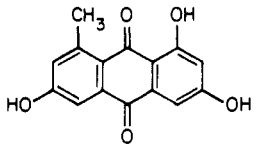
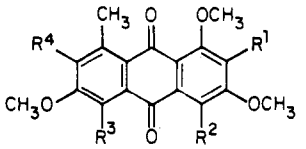
A regiospecific method of obtaining various quinones bearing at least three adjacent hydroxyl groups has been devised by using a new vinylketene acetal, 2-methoxy-1,1,3-tris(trimethylsiloxy)-1,3-butadiene (**9b**). In this way the first total syntheses of dermoglaucin (**50**) and ceroalbolinic acid, as its pentamethyl derivative **49**, have been achieved. The structure of another natural product, copareolatin dimethyl ether, was established indirectly by the unambiguous formation of one of the two possible isomers. Advantageous preparations of "7-hydroxyemodin", copareolatin, and isoerythrolaccin derivatives **32**, **38**, and **2**, as well as those of useful intermediates such as 2- and 3-chloro-5,7-dihydroxy-6-methoxynaphthoquinones or their dimethyl ethers, are described.

Some 1,2,3-trihydroxyanthraquinones such as "7-hydroxyemodin"[2] (**27**), isoerythrolaccin[2] (**44**) and copareolatin[3] (**37**) have been prepared by Friedel–Crafts-type condensations of the appropriate substrates; however, these reactions provide no regiochemical control over products and, except in the case of the parent compound anthragallol,[4] give complex mixtures in low yield. The method has limited value in establishing proof of structure, particularly if partially methylated substances are considered, and in one attempted synthesis[5] of ceroalbolinic acid gave only the wrong isomer.

A solution to some of the problems was proposed[6] recently and consists of the persulfate oxidation of a corresponding 1,3-dihydroxyanthraquinone. In this way "7-hydroxyemodin" was obtained from emodin with 20–33% conversion. When this method was applied to deoxyerythrolaccin (**1**), at least six products, besides starting



1



2 $R^1 = OCH_3$, $R^2 = R^3 = R^4 = H$

3 $R^1 = R^2 = H$, $R^3 = R^4 = OCH_3$

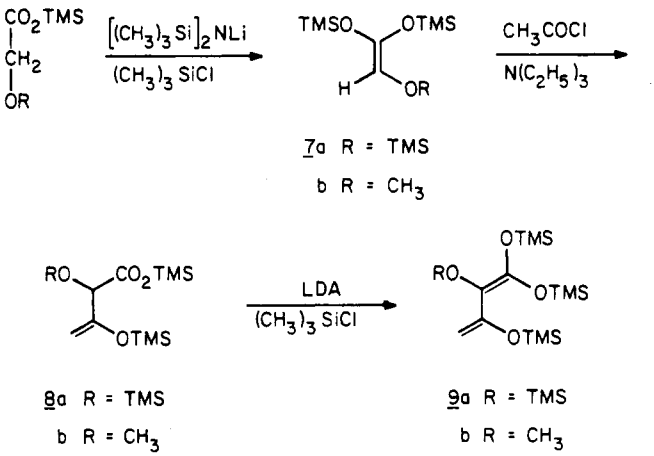
4 $R^1 = R^2 = R^4 = H$, $R^3 = OCH_3$

5 $R^1 = R^3 = R^4 = H$, $R^2 = OCH_3$

6 $R^1 = R^4 = H$, $R^2 = R^3 = OCH_3$

material (2%), were isolated after methylation of the crude mixture. Five of the compounds (as their permethylated derivatives) could be recognized as known substances or could readily be identified from their spectral characteristics: isoerythrolaccin, the desired product (**2**, 3%), 7-hydroxyerythrolaccin (**3**, 5%), erythrolaccin (**4**, 7%), 4-hydroxydeoxyethrythrolaccin (**5**, 8%), 4-hydroxyerythrolaccin (**6**, 3%), and a small amount of an unidentified compound. Since this reaction was carried out, the originators of the procedure have also applied it to deoxyerythrolaccin with unsatisfactory results.[6b]

Scheme I



7a R = TMS

b R = CH_3

8a R = TMS

b R = CH_3

9a R = TMS

b R = CH_3

An advantageous method of synthesis seemed available through the appropriate derivatives of vinylketene acetal since such dienes have recently been used efficiently, and in some cases regiospecifically, in reactions with quinones[7] and other dienophiles.[8] Various approaches to the elaboration of this type of synthon such as the preparation and dienolization of 2,3-dioxobutanal dimethyl acetal, the formation and electrocyclic ring opening of 1,2-bis(trimethylsiloxy)-3,3-dimethoxycyclobutene, or the synthesis and enolization of 2-oxo-3-methoxy-3-butenal dimethyl

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(2) V. B. Patil, A. V. Rama Rao, and K. Venkataraman, *Indian J. Chem.*, 8, 109 (1970).
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(4) C. Seuberlich, *Ber.*, 10, 38 (1877).
(5) D. D. Gadgil, A. V. Rama Rao, and K. Venkataraman, *Tetrahedron Lett.*, 2229 (1968).
(6) (a) H. J. Banks, D. W. Cameron, and M. J. Crossley, *Aust. J. Chem.*, 29, 2231 (1976); (b) H. J. Banks, D. W. Cameron, and W. D. Raverty, *ibid.*, 31, 2271 (1978).
(7) (a) J. Banville and P. Brassard, *J. Chem. Soc., Perkin Trans. 1*, 1852 (1976), and subsequent papers; (b) R. K. Boeckman, Jr., M. H. Delton, T. M. Dolak, T. Watanabe, and M. D. Glick, *J. Org. Chem.*, 44, 4396 (1979).
(8) (a) S. Danishefsky, C.-F. Yan, R. K. Singh, R. B. Gammill, P. M. McCurry, Jr., N. Fritsch, and J. Clardy, *J. Am. Chem. Soc.*, 101, 7001 (1979), and subsequent papers; (b) K. Yamamoto, S. Suzuki, and J. Tsuji, *Chem. Lett.*, 649 (1978); (c) R. Gompper and R. Sobotta, *Tetrahedron Lett.*, 921 (1979).

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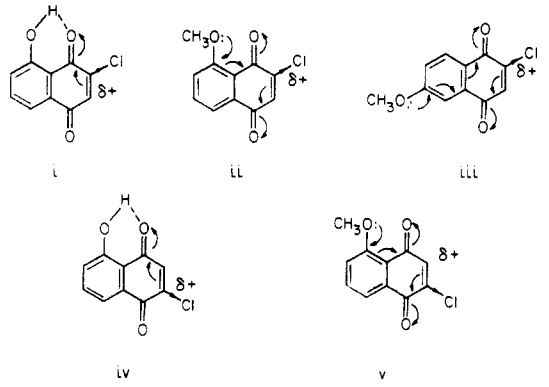
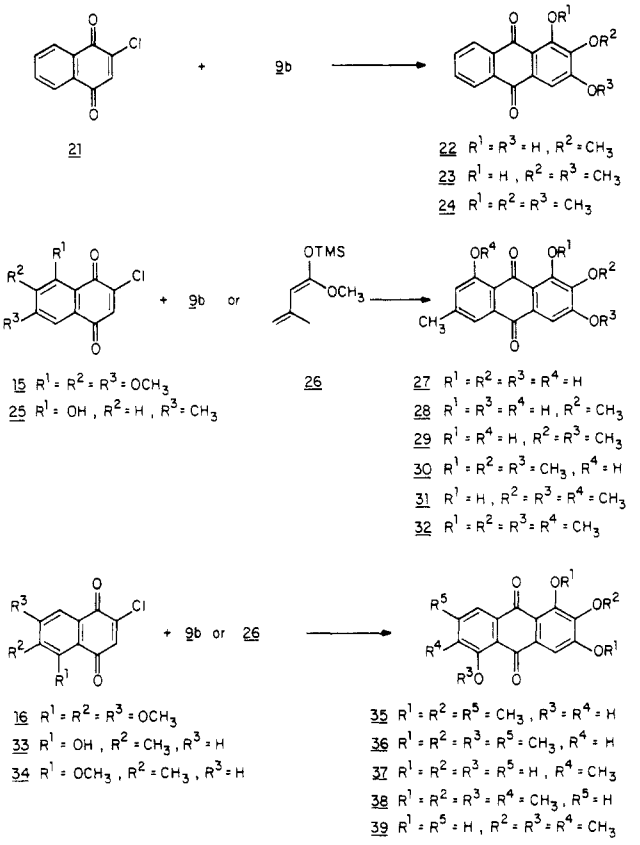
Chart I



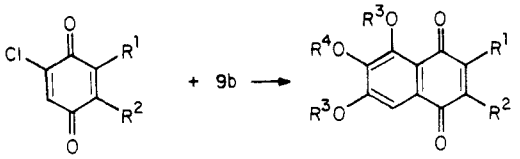
Scheme II



acetal either gave negative results or proved to be impractical. Eventually 1,1,2-tris(trimethylsiloxy)ethene (**7a**) and 2-methoxy-1,1-bis(trimethylsiloxy)ethene (**7b**) were prepared (Scheme I) according to the general procedure of Wissner,[9] and in the presence of ketene prepared in situ these compounds gave the expected[10] trimethylsilyl 2,3-bis(trimethylsiloxy)- and 2-methoxy-3-(trimethylsiloxy)-3-butenoates (**8a** and **8b**), respectively, which could then be enolized and converted to the corresponding dienes **9a** and **9b** in overall high yield.[11]

1,1,2-Tris(trimethylsiloxy)ethene (**7a**) reacted readily with benzoquinones as do other ketene acetals, but intermediates could not be converted to the usual products,[12] benzofurans or naphthoquinones. On the other hand, 1,1,2,3-tetrakis(trimethylsiloxy)-1,3-butadiene (**9a**) added slowly to dichlorobenzoquinones **10** or **11** but the adducts did not aromatize to trihydroxynaphthoquinones, except occasionally in very low yield under the conditions required for elimination. The diene did, however, form the desired regiospecific product with a limited number of chloronaphthoquinones,[1] but not with their 6-methoxy derivatives (e.g., **40**).

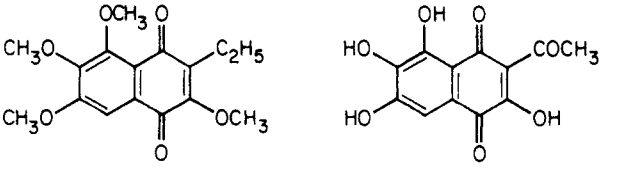
2-Methoxy-1,1,3-tris(trimethylsiloxy)butadiene (**9b**) also combined slowly with 2,6-dichlorobenzoquinone (**10**) but in contrast gave a good yield (79%) of the useful synthetic intermediate 3-chloro-5,7-dihydroxy-6-methoxynaphthoquinone (**14**) or, after methylation, of the trimethyl ether



10 $R^1 = Cl, R^2 = H$
11 $R^1 = H, R^2 = Cl$
12 $R^1 = OCH_3, R^2 = H$
13 $R^1 = H, R^2 = OCH_3$

14 $R^1 = Cl, R^2 = R^3 = H, R^4 = CH_3$
15 $R^1 = Cl, R^2 = H, R^3 = R^4 = CH_3$
16 $R^1 = H, R^2 = Cl, R^3 = R^4 = CH_3$
17 $R^1 = OCH_3, R^2 = H, R^3 = R^4 = CH_3$
18 $R^1 = H, R^2 = OCH_3, R^3 = R^4 = CH_3$

15. Additions of diene **9b** to the less electrophilic 2-chloro-5- (**13**) and -6-methoxybenzoquinones (**12**) must be conducted without solvent and produce only rather poor yields (18–29%) of the corresponding tetramethoxynaphthoquinones **18** and **17** after methylation. However, the latter can be obtained more efficiently by methoxide substitution of the corresponding chloro compounds **16** and **15**. Since 2,5,6,7-tetramethoxynaphthoquinone (**18**) had previously been converted to lomandrone 5-methyl ether[13] (**19**) and to spinochrome S[14] (**20**), this procedure constitutes a new and improved synthesis of these natural products.



19 **20**

Reactive naphthoquinones such as 2-chloronaphthoquinone (**21**) or 3-chlorojuglones (e.g., **25**) in which electron-donating groups in unfavorable positions (i.e., 6,8 and 5,7, respectively) are either absent or counterbalanced by hydrogen bonding[15] (i, Chart I) condense smoothly with diene **9b**, giving very good yields of the corresponding 2-*O*-methylanthragallols or, after etherification of the crude product, of their permethylated derivatives.

Use of a juglone ether (ii) as substrate, in which the unsubstituted carbon does not coincide with the site of greatest electron deficiency, decreases the rate and efficiency of the process to a point where only 12% of

(9) A. Wissner, *Tetrahedron Lett.*, 2749 (1978); *J. Org. Chem.*, 44, 4617 (1979).
(10) G. S. Burlachenko, Y. I. Baukov, and I. F. Lutsenko, *Zh. Obshch. Khim.*, **35**, 933 (1965); I. F. Lutsenko, Y. I. Baukov, G. S. Burlachenko, and B. N. Khasapov, *J. Organomet. Chem.*, **5**, 20 (1966); C. Ainsworth, F. Chen, and Y.-N. Kuo, *ibid.*, **46**, 59 (1972); C. Ainsworth and Y.-N. Kuo, *ibid.*, **46**, 73 (1972); M. W. Rathke and D. F. Sullivan, *Tetrahedron Lett.*, 1297 (1973).
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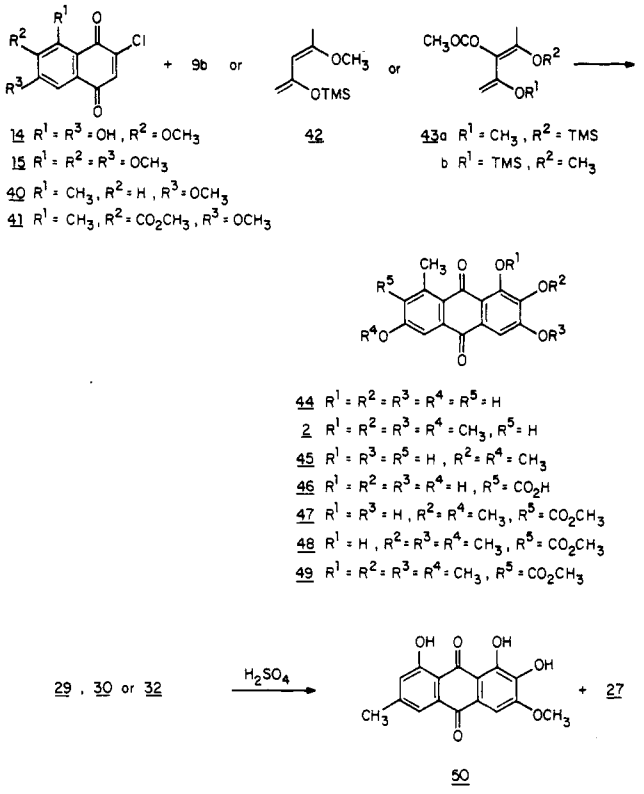
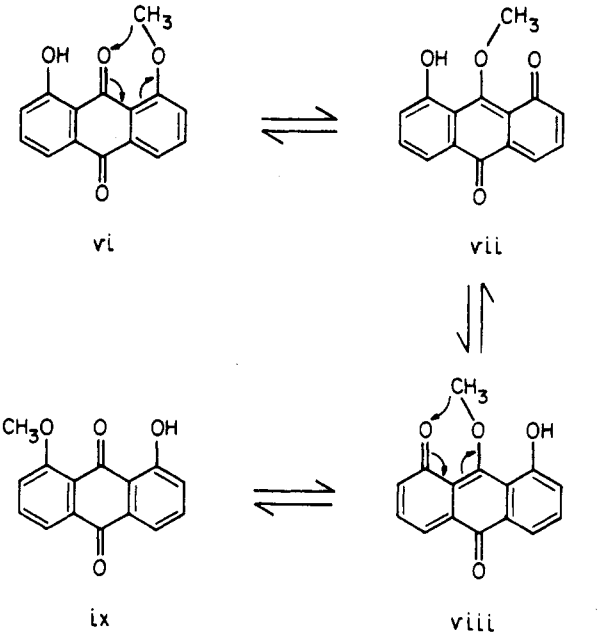
(14) J. W. Mathieson and R. H. Thomson, *J. Chem. Soc. C*, 153 (1971).
(15) R. H. Thomson, *J. Chem. Soc.*, **16**, 1082 (1951); R. K. Boeckman, Jr., T. M. Dolak, and K. O. Culos, *J. Am. Chem. Soc.*, **100**, 7098 (1978), and references therein.

Scheme III



Scheme IV



"tetra-*O*-methyl-7-hydroxyemodin" (**32**, Scheme II) could be obtained from 3-chloro-5-methoxy-7-methylnaphthoquinone[11] (after 55 days at 80 °C). 2-Chloronaphthoquinones methoxylated in the 6-position (iii) behave similarly; thus 2-chloro-6-methoxy-8-methylnaphthoquinone[16] (**40**) gave an isoerythrolaccin derivative (**45**, Scheme III) in only 24% yield after 34 days at 50 °C (even after 56 days, a conversion of only 41% could be ascertained). Introduction of electron-attracting substituents into naphthoquinone counteracts this effect to a certain extent so that 3-chloro-7-methoxy-6-(methoxycarbonyl)-5-methylnaphthoquinone[16] (**41**) could be converted to the ceroalbolinic acid derivative **47** in 40% yield after 13 days at 100 °C (a yield of 9% was obtained from the demethoxycarbonyl analogue **40** under similar conditions).

The slight reactivity observed with 3-chloro-5-methoxy- and 2-chloro-6-methoxynaphthoquinones also was shown by 2-chlorojuglone (iv) but to a lesser extent, as expected, since deactivation by a methoxyl group should in principle be greater than that of a peri hydroxyl function in which the unfavorable effect is merely reversed as a result of chelation.[15] This prediction was borne out by the preparation of copareolatin tetramethyl ether (**38**), in 93% yield, by a process that was complete in 7 days in refluxing benzene.

In 2-chloro-5-methoxynaphthoquinones (e.g., **34**) the electron deficiency again occurs in a favorable position (v), and copareolatin 2,5-dimethyl ether (**39**) was prepared from it in quantitative yield, cycloaddition being essentially complete in 24 h at 80 °C. This compound corresponds to one of the two structures deemed possible for a naturally occurring derivative of copareolatin.[17] The authentic material, though unavailable, seems to be quite different from the synthetic isomer (i.e., a 45 °C discrepancy in melting points). This therefore establishes the natural product as the alternative 1,2-dimethyl ether. Although these types of cycloadditions are generally treated as pericyclic reactions, the preceeding results and other observations are not inconsistent with a stepwise process as it has been acknowledged in the case of nonconjugated ketene acetals.[18]

The convergent approach used in these syntheses allows comparison of the foregoing procedures with the inverse sequence of annulations, which in some instances improves the overall process. In this perspective 3-chloro-5,7-dihydroxy-6-methoxynaphthoquinone (**14**) and its dimethyl ether **15** react slowly but quite comparably with the previously prepared 4-methoxy-2-(trimethylsiloxy)pentadiene[16] (**42**), giving 81 and 62% yields of tetra-*O*-methylisoerythrolaccin (**2**). In analogous reactions, the less nucleophilic 3-(methoxycarbonyl)-4-methoxy-2-(trimethylsiloxy)pentadiene[16] (**43b**) combined very slowly with naphthoquinone **15**, giving the ceroalbolinic acid derivative **49** in only 28% yield after 52 days, while the isomeric 2-methoxy-4-(trimethylsiloxy)pentadiene (**43a**) proved to be completely unreactive. Both foregoing dienes reacted equally well though extremely slowly with naphthoquinone **14** (~75%). The original sequence was found to be the more satisfactory for the preparation of "7-hydroxyemodin" derivatives.

Finally, the synthesis of dermoglaucin (**50**) was envisaged from 1,3,8-trihydroxy-2-methoxy-6-methylanthraquinone (**28**) by partial methylation followed by selective ether cleavage according to the method of Takido[20] (Scheme III). Methylation of the monoether **28** with methanol-free diazomethane gave the expected 2,3-dimethyl ether **29** and a trimethyl derivative identified as the 1,2,3-tri-*O*-methyl compound **30** since it was identical with the major product obtained from a condensation between 3-chloro-5,6,7-trimethoxynaphthoquinone (**15**) and diene **26**.[11] This reaction also produced the usual tetramethyl ether **32** and an unexpected substance which can only be the product of a novel type of rearrangement [(probably a double 1,5

(16) G. Roberge and P. Brassard, *J. Chem. Soc., Perkin Trans. 1*, 1041 (1978).
(17) L. H. Briggs, G. A. Nicholls, and R. M. L. Paterson, *J. Chem. Soc.*, 1718 (1952).
(18) R. Huisgen and G. Steiner, *Tetrahedron Lett.*, 3763 (1973).
(19) D. W. Cameron, G. I. Feutrill, P. G. Griffiths, and D. J. Hodder, *J. Chem. Soc., Chem. Commun.*, 688 (1978) (for the ethyl ester analogue).
(20) M. Takido, *Chem. Pharm. Bull.*, 8, 246 (1960).

methyl shift (vi → ix, Scheme IV)], the 2,3,8-trimethyl ether **31** since it was different from the 1,2,3-trimethoxy-5-hydroxy isomer **35**, isolated as the principal product from the reaction of 2-chloro-5,6,7-trimethoxynaphthoquinone (**16**) with the same diene.

Various derivatives of 1,2,3,8-tetrahydroxy-6-methylanthraquinone ("7-hydroxyemodin", **27**), the 2,3-dimethyl ether **29**, the 1,2,3-trimethyl ether **30**, and the tetramethyl ether **32** were selectively demethylated in concentrated sulfuric acid and gave dermoglaucin (**50**) as well as "7-hydroxyemodin" in various yields and proportions. However, the 2,3-dimethyl ether **29** affords the most satisfactory result, a 74% conversion to dermoglaucin.

Experimental Section

All melting points were taken for samples in capillary tubes with a Thomas-Hoover apparatus and a calibrated thermometer. The IR spectra were determined on a Beckman Model IR-12 spectrophotometer, NMR spectra were recorded with a Bruker HX-90 spectrometer using tetramethylsilane as an internal standard. Mass spectra were obtained with a Varian M-66 spectrometer. Woelm silica gel, activity III, for dry-column chromatography was used throughout, unless otherwise indicated, in a product to adsorbent ratio of 1:50.

Oxidation of 1,3,6-Trihydroxy-8-methylanthraquinone (Deoxyerythrolaccin, 1). Deoxyerythrolaccin (200 mg, 0.74 mmol) was oxidized by potassium persulfate according to the procedure used for emodin.[6] Methylation of the crude product in the usual way [$(CH_3)_2SO_4$, K_2CO_3, acetone, 24 h] gave a mixture of at least six products which were separated by preparative TLC (benzene–ethyl acetate, 10:1, two migrations) into four main zones.

A fast-moving band, after purification by the same process, gave isoerythrolaccin tetramethyl ether [**2**: 7 mg (3%); mp 176–177 °C (methanol) (lit.[21] mp 176–177 °C), identical with a substance prepared subsequently.

A second fraction, separated by TLC (chloroform–ethyl acetate, 20:1), yielded the derivative of the starting material, 1,3,6-trimethoxy-8-methylanthraquinone (4 mg , 2%) and 1,3,5,6,7-pentamethoxy-8-methylanthraquinone (**3**): 14 mg (5%); mp 197–199 °C (methanol); IR ν_{max} (KBr) 1659, 1598, 1577 (br) cm^{-1}; NMR ($CDCl_3$) δ 2.72 (3 H, s, 8-CH_3), 3.87, 3.97, 4.00, and 4.02 (15 H, 4 s, 1,3,5,6,7-OCH_3), 6.78 (1 H, d, J = 2.5 Hz, 2-H), 7.36 (1 H, d, J = 2.5 Hz, 4-H); mass spectrum, m/e 372 (M^+).

The third zone provided erythrolaccin tetramethyl ether [**4**: 18 mg (7%); mp 158–160 °C (methanol) (lit.[22] mp 159 °C)], which was found to be identical with the substance obtained earlier by an unambiguous procedure.[23]

A final band, also resolved by preparative TLC (chloroform–methanol, 200:1), gave 1,3,4,6-tetramethoxy-8-methylanthraquinone [**5**: 19 mg (8%); mp 165–166 °C (methanol)], identical with a substance prepared for this purpose (vide infra), an unidentified substance (9 mg), and 1,3,4,5,6-pentamethoxy-8-methylanthraquinone (**6**): 9 mg (3%); mp 154–157 °C (methanol); IR ν_{max} (KBr) 1677, 1671, 1586 cm^{-1}; NMR ($CDCl_3$) δ 2.70 (3 H, s, 8-CH_3), 3.96 and 3.98 (6 H and 9 H, 2 s, 1,3,4,5,6-OCH_3), 6.71 (1 H, s, 2-H), 6.91 (1 H, s, 7-H); mass spectrum, m/e 372 (M^+).

1,3,4,6-Tetramethoxy-8-methylanthraquinone (5). A solution of 1,1,4-trimethoxy-3-(trimethylsiloxy)-1,3-butadienes[24] (696 mg, 3.00 mmol) in anhydrous benzene (10 mL) was added to 2-chloro-6-methoxy-8-methylnaphthoquinone[16] (**40**; 473 mg, 2.00 mmol) in the same solvent, and the mixture was refluxed for 72 h [another portion of dienes (2.00 mmol in 5 mL of solvent) was added after 48 h]. The residue after evaporation was heated at 130–135 °C for 2.5 h and methylated in the usual way. The tetramethyl ether was then isolated by chromatography (chloroform): 570 mg (83%); mp 165–166 °C (methanol); IR ν_{max} (KBr) 1661, 1598, 1583 cm^{-1}; NMR ($CDCl_3$) δ 2.77 (3 H, s, 8-CH_3), 3.92, 3.97, 4.00, and 4.03 (4 × 3 H, 4 s, 1,3,4,6-OCH_3), 6.82 (1 H, s, 2-H), 6.99 (1 H, d, J = 2.5 Hz, 7-H), 7.51 (1 H, d, J = 2.5 Hz, 5-H). Anal. Calcd for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30. Found: C, 66.85; H, 5.37.

Trimethylsilyl 2-Methoxy-3-(trimethylsiloxy)but-3-enoate (8b). Acetyl chloride (15.8 g, 0.20 mol) in anhydrous ether (100 mL) was added slowly (2.5 h) to a mixture of 2-methoxy-1,1-bis(trimethylsiloxy)ethene[9] (**7b**; 46.9 g, 0.20 mol) and dry triethylamine (20.4 g, 0.20 mol) in the same solvent (200 mL). The reaction mixture was stirred at room temperature (2 h), filtered, and concentrated. Distillation of the residue under vacuum gave the ester **8b**: 49.6 g (89%); bp 62–66 °C (0.4 mmHg); IR ν_{max} (film) 1733 and 1717 (C=O), 1643 (C=C), 842 (SiC) cm^{-1}; NMR ($CDCl_3$) δ 0.23 and 0.31 (2 × 9 H, 2 s, $OSi(CH_3)_3$), 3.38 (3 H, s, 2-OCH_3), 4.03 (1 H, s, 2-H), 4.31 (1 H, d, J = 1.5 Hz, 4-H), 4.41 (1 H, d, J = 1.5 Hz, 4-H). Anal. Calcd for $C_{11}H_{24}O_4Si_2$: C, 47.78; H, 8.75. Found: C, 47.66, H, 8.79.

2-Methoxy-1,1,3-tris(trimethylsiloxy)-1,3-butadiene (9b). To a solution of lithium diisopropylamide, prepared from *n*-butyllithium (0.075 mol) in hexane (1.6 M, 46.5 mL) and dry diisopropylamine (7.65 g, 0.075 mol) in anhydrous tetrahydrofuran (75 mL) at 4 °C (30 min), was added below −65 °C (90 min) trimethylsilyl 2-methoxy-3-(trimethylsiloxy)but-3-enoate (**8b**; 20.7 g, 0.075 mol) in tetrahydrofuran (75 mL). The solution was stirred at −70 °C for 30 min and the enolate quenched by addition of chlorotrimethylsilane (20.4 g, 0.188 mol) between −65 and −70 °C (30 min). After being stirred at −65 °C for 30 min, the reaction mixture was allowed to come to room temperature, concentrated, diluted with petroleum ether, bp 30–60 °C (250 mL) and filtered. The solids were washed with the same solvent (450 mL) and the combined filtrates evaporated. Distillation of the residue gave diene **9b**: 23.1 g (88%); bp 68–72 °C (0.08 mmHg); IR ν_{max} (film) 1649 and 1593 (diene), 840 (SiC) cm^{-1}; NMR ($CDCl_3$) δ 0.21, 0.23, and 0.26 (3 × 9 H, 3 s, 1,1,3-$OSi(CH_3)_3$), 3.38 (3 H, s, 2-OCH_3), 4.29 (1 H, s, 4-H), 4.49 (1 H, s, 4-H). Anal. Calcd for $C_{14}H_{32}O_4Si_3$: C, 48.23; H, 9.25. Found: C, 48.09; H, 9.39.

Reactions of 2-Methoxy-1,1,3-tris(trimethylsiloxy)butadiene (9b) and Other Dienes with Chloroquinones. Method A. A benzene solution of the diene and the quinone was refluxed and evaporated. The residue was heated at the appropriate temperature (110–130 °C) for the required time (1–3 h) as determined by the evolution of HCl and then hydrolyzed by being warmed at 50 °C for a few minutes with a 1:1 mixture of THF and 2% aqueous HCl (20 mL/mmol of quinone). The crude product could then be isolated by chromatography or methylated (either partially or completely).

Method B was the same as for A but without pyrolysis.

Method C was the same as for B but with cycloaddition carried out at room temperature.

Method D was the same as for B but with cycloaddition conducted at 50 °C in the absence of solvent.

Method E was the same as for the D but with condensation carried out at 100 °C.

3-Chloro-5,7-dihydroxy-6-methoxynaphthoquinone (14). The residue obtained from the reaction of 2,6-dichlorobenzoquinone (**10**; 1.770 g, 10.00 mmol) and butadiene **9b** (3.835 g, 11.00 mmol) by use of method B (4 days) was purified by chromatography (benzene–ethyl acetate, 40:1, or chloroform) and gave naphthoquinone **14**: 2.017 g (79%); mp 192–193 °C (benzene); IR ν_{max} (KBr) 3400, 1661, 1640 br, 1594, 1581, 1265 (br) cm^{-1}; NMR ($CDCl_3$) δ 4.08 (3 H, s, 6-OCH_3), 6.44 (1 H, br s, 7-OH), 7.09 (1 H, s, 2-H), 7.24 (1 H, s, 8-H), 12.10 (1 H, br s, 5-OH). Anal. Calcd for $C_{11}H_7ClO_5$: C, 51.89; H, 2.77; Cl, 13.93. Found: C, 51.95; H, 2.85; Cl, 13.92.

3-Chloro-5,6,7-trimethoxynaphthoquinone (15). Methylation (for naphthoquinones: CH_3I, Ag_2O-$CHCl_3$, 1.5 days, room temperature) of the crude product prepared from quinone **10** (354 mg, 2.00 mmol) and diene **9b** (767 mg, 2.20 mmol) after 14 days (method C) gave the trimethyl ether **15**, isolated by chromatography (benzene): 378 mg (67%); mp 146–147 °C (carbon tetrachloride); IR ν_{max} (KBr) 1670, 1604, 1574, 1262 cm^{-1}; NMR ($CDCl_3$) δ 3.97, 3.98, and 4.03 (3 × 3 H, 3 s, 5,6,7-OCH_3), 7.12 (1 H, s, 2-H), 7.47 (1 H, s, 8-H). Anal. Calcd for $C_{13}H_{11}ClO_5$: C, 55.23; H, 3.92; Cl, 12.54. Found: C, 55.25; H, 3.90; Cl, 12.52.

2-Chloro-5,6,7-trimethoxynaphthoquinone (16). An analogous reaction (method B, 8 days) with 2,5-dichlorobenzoquinone (**11**, 10 mmol) and diene **9b** (11 mmol), after methylation and chromatography (benzene), gave naphthoquinone **16**: 1.606 g

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(57%); mp 152–153 °C (benzene–petroleum ether, bp 30–80 °C); IR ν_{max} (KBr) 1673, 1655, 1611, 1574, 1285 cm^{-1}; NMR ($CDCl_3$) δ 3.93, 3.98, and 4.03 (3 × 3 H, 3 s, 5,6,7-OCH_3), 7.04 (1 H, s, 3-H), and 7.52 (1 H, s, 8-H). Anal. Calcd for $C_{13}H_{11}ClO_5$: C, 55.23; H, 3.92; Cl, 12.54. Found: C, 55.52; H, 3.99; Cl, 12.29.

3,5,6,7-Tetramethoxynaphthoquinone (17). The condensation (method D, 7 days) of 2-chloro-6-methoxybenzoquinone[25] (**12**; 345 mg, 2.00 mmol) with diene **9b** (2.20 mmol), after methylation and chromatography (benzene–ethyl acetate, 20:1), yielded the tetramethyl ether **17**: 162 mg (29%) mp 180–182 °C (benzene–hexane) (lit.[26] mp 185–187 °C); IR ν_{max} (KBr) 1678, 1650, 1616, 1577, 1264, 1235 cm^{-1}; NMR ($CDCl_3$) δ 3.93, 3.99, 4.00, 4.07 (4 × 3 H, 4 s, 3,5,6,7-OCH_3), 6.12 (1 H, s, 2-H), 7.54 (1 H, s, 8-H); mass spectrum, m/e 278 (M^+). Anal. Calcd for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07. Found: C, 60.62; H, 5.00. This substance and an authentic sample were indistinguishable by the usual criteria.

The same compound **17** was obtained by substitution of 3-chloro-5,6,7-trimethoxynaphthoquinone (**15**; 141 mg, 0.50 mmol) using freshly prepared sodium methoxide (two portions of 33 mg, 0.60 mmol, each) in benzene (10 mL; 7 days); yield 83 mg (60%).

2,5,6,7-Tetramethoxynaphthoquinone (18). By an analogous process (method D, 4 days) using 2-chloro-5-methoxybenzoquinone[25] (**13**; 345 mg, 2.00 mmol) and diene **9b** (3.00 mmol), a mixture of starting material (44 mg, 13%) and the desired product **18** [99 mg (18%); mp 178–179 °C (benzene) (lit. mp 187–189 °C,[26] 185–186 °C[13])] were obtained after methylation and separated by chromatography (benzene then benzene–ethyl acetate, 10:1): IR ν_{max} (KBr) 1673, 1646, 1621, 1576, 1250, 1231 cm^{-1}; NMR ($CDCl_3$) δ 3.91, 3.98, 4.04, 4.08 (4 × 3 H, 4 s, 2,5,6,7-OCH_3), 6.09 (1 H, s, 3-H), 7.60 (1 H, s, 8-H); mass spectrum m/e 278 (M^+). Anal. Calcd for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07. Found: C, 60.50; H, 5.13. This compound and the authentic material were indistinguishable by the usual standards.

Substitution of 2-chloro-5,6,7-trimethoxynaphthoquinone (0.50 mmol) by methoxide as in the preceding section gave the same tetramethyl ether **18** (eluted with benzene), 52 mg (37%).

1,3-Dihydroxy-2-methoxyanthraquinone (22). The crude product obtained (method B, 18 days) from 2-chloronaphthoquinone (**21**; 963 mg, 5.00 mmol) and diene **9b** (7.50 mmol), after purification by chromatography (benzene–ethyl acetate, 10:1), gave the anthraquinone **22**: 1.209 g (90%); mp 219–220 °C (dioxane) (lit. mp 218–220 °C,[27] 220 °C[28]); IR ν_{max} (KBr) 3450, 3420, 1666, 1634, 1592, 1582, 1262 cm^{-1}; NMR [$(CD_3)_2SO$] δ 3.86 (3 H, s, 2-OCH_3), 7.22 (1 H, s, 4-H), 7.78–8.00 (2 H, m, 6,7-H), 8.00–8.23 (2 H, m, 5,8-H), 12.83 (1 H, br s, 1-OH); mass spectrum, m/e 270 (M^+). Anal. Calcd for $C_{15}H_{10}O_5$: C, 66.67; H, 3.73. Found: C, 66.71; H, 3.84.

Methylation at −5 °C (4 days) of the foregoing compound **22** (540 mg, 2.00 mmol) in anhydrous ether (500 mL) by addition of diazomethane (840 mg, 20.00 mmol) in the same solvent (100 mL) gave, after chromatography (benzene), 1-hydroxy-2,3-dimethoxyanthraquinone (**23**): 297 mg (52%); mp 162–163 °C (absolute ethanol) (lit.[29] mp 166–167 °C); IR ν_{max} (KBr) 1667, 1634, 1591, 1576, 1275 cm^{-1}; NMR ($CDCl_3$) δ 4.01 (6 H, s, 2,3-OCH_3), 7.34 (1 H, s, 4-H), 7.67–7.81 (2 H, m, 6,7-H), 8.06–8.23 (2 H, m, 5,8-H), 12.68 (1 H, s, 1-OH). Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.26. Found: C, 67.84; H, 4.39. A second fraction consisted of 1,2,3-trimethoxyanthraquinone (**24**), 118 mg (20%).

When the residue obtained from a similar reaction (method E, 36 h) between 2-chloronaphthoquinone (**21**, 2.00 mmol) and diene **9b** (3.00 mmol) was methylated [$(CH_3)_2SO_4$, K_2CO_3, acetone, 18 h], chromatographic purification (benzene–ethyl acetate, 20:1) gave the trimethyl ether **24**: 495 mg (83%); mp 171–172 °C (acetone).

1,3,8-Trihydroxy-2-methoxy-6-methylanthraquinone (28). The residue obtained from the reaction of 3-chloro-5-hydroxy-7-methylnaphthoquinone[11] (**25**; 446 mg, 2.00 mmol) and butadiene **9b** (1.396 g, 4.00 mmol) by method A (5 days) after pyrolysis at 110 °C (2 h) and chromatography (benzene–ethyl acetate, 10:1) gave the monomethyl ether **28**: 523 mg (87%); mp 270–275 °C dec; IR ν_{max} (KBr) 3330, 1655, 1629, 1606, 1575, 1266 cm^{-1}; NMR [$(CD_3)_2SO$] δ 2.31 (3 H, s, 6-CH_3), 3.87 (3 H, s, 2-OCH_3), 6.96 (1 H, br s, 7-H), 7.08 (1 H, s, 4-H), 7.23 (1 H, d, J = 2.0 Hz, 5-H), 11.76 and 12.06 (2 × 1 H, 2 s, 1,8-OH).

Methylation of the foregoing compound (900 mg, 3.00 mmol) with diazomethane (30.00 mmol) in ether (600 mL) (6 h at 2 °C and 12 h at room temperature) gave 1,8-dihydroxy-2,3-dimethoxy-6-methylanthraquinone (**29**; 428 mg, 45%) after chromatography (carbon tetrachloride): mp 198–199 °C (methanol) (lit. mp 188–190 °C,[21] 192 °C[30]); IR ν_{max} (KBr) 1664, 1627, 1603, 1563, 1242 cm^{-1}; NMR ($CDCl_3$) δ 2.42 (3 H, s, 6-CH_3), 4.02 and 4.06 (2 × 3 H, 2 s, 2,3-OCH_3), 7.01 (1 H, br s, 7-H), 7.37 (1 H, s, 4-H), 7.52 (1 H, d, J = 1.5 Hz, 5-H), 11.91 and 12.17 (2 × 1 H, 2 s, 1,8-OH). Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.96; H, 4.49. Found: C, 65.15; H, 4.65. Benzene elutes 8-hydroxy-1,2,3-trimethoxy-6-methylanthraquinone (**30**; 135 mg, 14%) identical with the compound prepared subsequently.

When the crude product from a similar condensation involving naphthoquinone **25** (1.00 mmol) and diene **9b** (2.00 mmol) (method A, 16 h) was pyrolyzed at 120 °C (2 h), hydrolyzed, and methylated in the usual way, 1,2,3,8-tetramethoxy-6-methylanthraquinone (**32**; 291 mg, 85%) was isolated after chromatography (benzene–ethyl acetate, 20:1) and was indistinguishable with a substance prepared previously.[1]

8-Hydroxy-1,2,3-trimethoxy-6-methylanthraquinone (30). The reaction of 3-chloro-5,6,7-trimethoxynaphthoquinone (**15**; 282 mg, 1.00 mmol) and 1-methoxy-3-methyl-1-(trimethylsiloxy)-1,3-butadiene[11] (**26**; 372 mg, 2.00 mmol) (method A, 6 h) followed by pyrolysis at 120 °C (2 h) and chromatography (benzene) gave as the principal product the expected 8-hydroxyanthraquinone **30**: 153 mg (46%) mp 195–196 °C (methanol); IR ν_{max} (KBr) 1660, 1639, 1580, 1272 cm^{-1}; NMR ($CDCl_3$) δ 2.41 (3 H, s, 6-CH_3), 4.01 and 4.06 (6 H and 3 H, 2 s, 1,2,3-OCH_3), 7.09 (1 H, br s, 7-H), 7.57 (1 H, d, J = 2.0 Hz, 5-H), 7.69 (1 H, s, 4-H), 12.99 (1 H, s, 8-OH). Anal. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91. Found: C, 65.64; H, 4.82. A second fraction (benzene–ethyl acetate, 40:1) consisted of the rearranged 1-hydroxy-2,3,8-trimethoxy-6-methylanthraquinone (**31**): 44 mg (13%); mp 199–201 °C (methanol); IR ν_{max} (KBr) 1669, 1640, 1603, 1590, 1252 cm^{-1}; NMR ($CDCl_3$) δ 2.46 (3 H, s, 6-CH_3), 4.01, 4.02, and 4.04 (3 × 3 H, 3 s, 2,3,8-OCH_3), 7.16 (1 H, br s, 7-H), 7.41 (1 H, s, 4-H), 7.77 (1 H, br s, 5-H), 13.26 (1 H, br s, 1-OH). Anal. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91. Found: C, 65.73; H, 4.90. A final zone (benzene–ethyl acetate, 10:1) yielded the corresponding tetramethyl ether **32** (118 mg, 34%) described previously.

5-Hydroxy-1,2,3-trimethoxy-7-methylanthraquinone (35). A similar condensation with 2-chloro-5,6,7-trimethoxynaphthoquinone (**16**, 1.00 mmol) and diene **26** (2.00 mmol) (method A, 1 h) after pyrolysis at 120 °C (1 h) and chromatography (benzene) yielded the 5-hydroxyanthraquinone **35**: 239 mg (73%); mp 163–164 °C (methanol); IR ν_{max} (KBr) 1660, 1640, 1600, 1578, 1268 cm^{-1}; NMR ($CDCl_3$) δ 2.46 (3 H, s, 7-CH_3), 4.03, 4.06, and 4.09 (3 × 3 H, 3 s, 1,2,3-OCH_3), 7.03 (1 H, br s, 6-H), 7.59 (1 H, br s, 8-H), 7.68 (1 H, s, 4-H), 12.41 (1 H, s, 5-OH). Anal. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91. Found: C, 65.91; H, 5.04. A second fraction (benzene–ethyl acetate, 20:1) gave the corresponding 1,2,3,5-tetramethoxy-7-methylanthraquinone (**36**): 74 mg (22%); mp 182–183 °C (methanol); IR ν_{max} (KBr) 1663, 1602, 1576, 1273 cm^{-1}; NMR ($CDCl_3$) δ 2.49 (3 H, s, 7-CH_3), 4.02, 4.03, 4.05, and 4.07 (4 × 3 H, 4 s, 1,2,3,5-OCH_3), 7.11 (1 H, br s, 6-H), 7.72 (1 H, s, 4-H), 7.75 (1 H, br s, 8-H). Anal. Calcd for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30. Found: C, 66.47; H, 5.35.

1,2,3,5-Tetramethoxy-6-methylanthraquinone (Tetra-*O*-methylcopareolatin, 38). The crude product obtained from the condensation of 2-chloro-5-hydroxy-6-methylnaphthoquinone[1] (**33**; 55 mg, 0.25 mmol) and butadiene **9b** (349 mg, 1.00 mmol) (method D, 7 days) was methylated in the usual way and after chromatography (benzene) gave the tetramethyl ether **38** (80 mg, 93%), identical with the substance prepared earlier.[1]

2-Chloro-5-methoxy-6-methylnaphthoquinone (34). Methylation of 2-chloro-5-hydroxy-6-methylnaphthoquinone in the usual way (for napthoquinones), and chromatography (carbon tetrachloride) gave the methyl ether **34**: 78%; mp 149–150 °C

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(petroleum ether, bp 30–80 °C); IR ν_{max} (KBr) 1665, 1610, 1584, 1274, 1240 cm^{-1}; NMR ($CDCl_3$) δ 2.33 (3 H, s, 6-CH_3), 3.76 (3 H, s, 5-OCH_3), 6.96 (1 H, s, 3-H), 7.42 (1 H, d, J = 8.0 Hz, 7-H), 7.73 (1 H, d, J = 8.0 Hz, 8-H).

1,3-Dihydroxy-2,5-dimethoxy-6-methylanthraquinone (2,5-Di-*O*-methylcopareolatin, 39). Reaction of this naphthoquinone **34** (59 mg, 0.25 mmol) and butadiene **9b** (1.00 mmol) (method A, 24 h) gave a crude adduct which was pyrolyzed at 50 °C (3 h) and yielded the dimethyl ether **39** by chromatography (benzene–ethyl acetate, 20:1): 78 mg (99%); mp 225–226 °C (methanol); IR ν_{max} (KBr) 3400 (br), 1660, 1631, 1585, 1260 cm^{-1}; NMR [$(CD_3)_2SO$] δ 2.29 (3 H, s, 6-CH_3), 3.73 and 3.80 (2 × 3 H, 2 s, 2,5-OCH_3), 7.09 (1 H, s, 4-H), 7.61 (2 H, dd, J = 8.0 Hz, $\Delta\nu$ = 4.1 Hz, 7,8-H). Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.96; H, 4.49. Found: C, 65.03; H, 4.58.

1,2,3,6-Tetramethoxy-8-methylanthraquinone (Isoerythrolaccin Tetramethyl Ether, 2). The product formed in the cycloaddition of 3-chloro-5,6,7-trimethoxynaphthoquinone (**15**; 283 mg, 1.00 mmol) to the mixture of 4-methoxy-2-(trimethylsiloxy)-1,3-pentadienes[16] (**42**; 1.116 g, 6.00 mmol; in three portions) (method A, 11 days) was pyrolyzed at 125 °C (3 h) and, after methylation and chromatography (benzene), gave the tetramethyl ether **2**: 212 mg (62%); mp 176–177 °C (methanol) (lit.[21] mp 176–177 °C); IR ν_{max} (KBr) 1663, 1606, 1579, 1274 cm^{-1}; NMR ($CDCl_3$) δ 2.72 (3 H, s, 8-CH_3), 3.89, 3.98, 4.00 (3 H, 3 H, and 6 H, 3 s, 1,2,3,6-OCH_3), 6.91 (1 H, d, J = 3.0 Hz, 7-H), 7.46 (1 H, d, J = 3.0 Hz, 5-H), 7.50 (1 H, s, 4-H); mass spectrum, m/e 342 (M^+). Anal. Calcd for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30. Found: C, 66.57; H, 5.32.

The same compound could be obtained from 3-chloro-5,7-dihydroxy-6-methoxynaphthoquinone (**14**; 255 mg, 1.00 mmol) and the same pentadienes **42** (4.00 mmol in two portions; method A, 22 days) after pyrolysis at 125 °C (1 h), methylation, and chromatography (benzene–ethyl acetate, 20:1) in 81% yield.

1,3-Dihydroxy-2,6-dimethoxy-8-methylanthraquinone (45) and 1,2,3,6-Tetrahydroxy-8-methylanthraquinone (Isoerythrolaccin, 44). The inverse sequence of addition with 2-chloro-6-methoxy-8-methylnaphthoquinone (**40**; 237 mg, 1.00 mmol) and butadiene **9b** (4.00 mmol in two portions) (method A, 56 days) after pyrolysis at 130 °C (1.5 h) and chromatography (benzene–ethyl acetate, 10:1) gave the dimethyl ether **45**: 128 mg (41%); mp 224–228 °C; IR ν_{max} (KBr) 3360 (Br), 1650, 1624, 1598, 1584, 1258 cm^{-1}; NMR [$(CD_3)_2SO$] δ 2.52 (3 H, s, 8-CH_3), 3.84 and 3.89 (2 × 3 H, 2 s, 2,6-OCH_3), 6.89 (1 H, d, J = 2.5 Hz, 7-H), 6.98 (1 H, s, 4-H), 7.07 (1 H, d, J = 2.5 Hz, 5-H), 10.70 (1 H, br s, 1-OH).

A mixture of the foregoing compound **45** (157 mg, 0.50 mmol) and pyridine hydrochloride (90 g) was heated at 160 °C for 16 h under nitrogen and after the usual workup and sublimation at 220 °C (0.5 mmHg) gave isoerythrolaccin **44**: 43 mg (30%); mp >320 °C dec (methanol) (lit.[21] mp >320 °C); IR ν_{max} (KBr) 3400 (br), 3300, 1628, 1595 cm^{-1}; NMR [$(CD_3)_2SO$] δ 2.70 (~3 H, s, 8-CH_3), 6.93 (1 H, d, J = 3.0 Hz, 7-H), 7.16 (1 H, s, 4-H), 7.39 (1 H, d, J = 3.0 Hz, 5-H).

8-Hydroxy-3,6,7-trimethoxy-2-(methoxycarbonyl)-1-methylanthraquinone (Methyl Ceroalbolinate 3,6,7-Trimethyl Ether, 48). The condensation of 3-chloro-7-methoxy-6-(methoxycarbonyl)-5-methyl-naphthoquinone[16] (**41**; 589 mg, 2.00 mmol) with diene **9b** (1.046 g, 3.00 mmol) (method E, 13 days), after chromatography (benzene) gave the starting material **41** (30 mg, 5%) and a second fraction (benzene–ethyl acetate, 10:1) consisting of 6,8-dihydroxy-3,7-dimethoxy-2-(methoxycarbonyl)-1-methylanthraquinone (**47**): 301 mg (40%); mp 230–235 °C; IR ν_{max} (KBr) 3410 (br), 1727, 1656, 1625, 1580, 1267 cm^{-1}; NMR [$(CD_3)_2SO$] δ 2.43 (3 H, s, 1-CH_3), 3.84, 3.89, and 3.97 (3 × 3 H, 3 s, 2-CO_2CH_3, 3,7-OCH_3), 7.02 (1 H, s, 5-H), 7.39 (1 H, s, 4-H), 10.89 (1 H, br s, 8-OH). The foregoing substance **47** (0.372 mg, 1.00 mmol) was methylated in the usual way (excess CH_2N_2, ether, −5 °C, 96 h) and after purification by chromatography (benzene) gave the trimethyl ether **48**: 298 mg (77%); mp 237–238 °C (chloroform–methanol) (lit.[31] mp 245–248 °C); IR ν_{max} (KBr) 1734, 1665, 1627, 1578, 1275 cm^{-1}; NMR ($CDCl_3$) δ 2.70 (3 H, s, 1-CH_3), 3.99 and 4.03 (3 H and 9 H, 2 s, 2-CO_2CH_3, 3,6,7-OCH_3), 7.38 (1 H, s, 5-H), 7.70 (1 H, s, 4-H), 13.11 (1 H, s, 8-OH). Anal. Calcd for $C_{20}H_{18}O_8$: C, 62.17; H, 4.70. Found: C, 62.38; H, 4.78.

3,6,7,8-Tetramethoxy-2-(methoxycarbonyl)-1-methylanthraquinone (Methyl Ceroalbolinate Tetramethyl Ether, 49). The products obtained from 3-chloro-5,7-dihydroxy-6-methoxynaphthoquinone (**14**; 450 mg, 2.00 mmol) and either the mixture of 2-methoxy-3-(methoxycarbonyl)-4-(trimethylsiloxy)-1,3-pentadienes[19] (**43a**) or that of 4-methoxy-3-(methoxycarbonyl)-2-(trimethylsiloxy)-1,3-pentadienes[16] (**43b**; 2.196 g, 9.00 mmols; added in three portions) (method A, 47 days) were pyrolyzed at 110 °C (2 h) and methylated and after chromatography (benzene–ethyl acetate, 20:1) gave the tetramethyl ether **49**: 600–606 mg (75–76%); mp 198–199 °C (methanol) (lit.[31] mp 201–204 °C); IR ν_{max} (KBr) 1728, 1663, 1582, 1259 cm^{-1}; NMR ($CDCl_3$) δ 2.72 (3 H, s, 1-CH_3), 4.01, 4.05, and 4.08 (3 H, 9 H, and 3 H, 3 s, 2-CO_2CH_3, 3,6,7,8-OCH_3), 7.63 (1 H, s, 5-H), 7.70 (1 H, s, 4-H); mass spectrum, m/e 400 (M^+). Anal. Calcd for $C_{21}H_{20}O_8$: C, 62.99; H, 5.04. Found: C, 63.06; H, 4.99. This substance and the derivative of the natural product were indistinguishable by the usual criteria.

1,2,8-Trihydroxy-3-methoxy-6-methylanthraquinone (Dermoglaucin, 50). The product obtained by heating 1,8-dihydroxy-2,3-dimethoxy-6-methylanthraquinone (**29**; 79 mg, 0.25 mol) in concentrated H_2SO_4 (10 mL) at 100 °C (1.5 h), pouring the mixture on ice (50 g), and stirring for 16 h gave dermoglaucin (**50**) after chromatography (benzene–ethyl formate, 9:1): 56 mg (74%); mp 235–236 °C (ethyl acetate) (lit.[30] mp 236 °C); IR ν_{max} (KBr) 3420 (br), 1660, 1623, 1574, 1272, 1226 cm^{-1}; NMR [$(CD_3)_2SO$] δ 2.36 (3 H, s, 6-CH_3), 3.89 (3 H, s, 6-OCH_3), 6.94 (1 H, d, J = 1.5 Hz, 7-H), 7.16 (1 H, s, 4-H), 7.29 (1 H, d, J = 1.5 Hz, 5-H). Anal. Calcd for $C_{16}H_{12}O_6$: C, 64.00; H, 4.03. Found: C, 63.78; H, 4.03. This compound and an authentic sample were indistinguishable according to the usual criteria. A second zone consisted 1,2,3,8-tetrahydroxy-6-methylanthraquinone ("7-hydroxyemodin",[1] **27**), 14 mg (19%).

A similar reaction using 8-hydroxy-1,2,3-trimethoxy-6-methylanthraquinone (**30**) gave 65% of **51** and 18% of **27** while 1,2,3,8-tetramethoxy-6-methylanthraquinone (**32**) was converted to **51** and **27** in yields of 34% and 57%, respectively.

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(31) T. Rios, *Tetrahedron*, **22**, 1507 (1966).