Reactions of Keten Acetals. Part VI.[1] Total Syntheses of the Anthraquinones (±)-Nalgiovensin, (±)-Isorhodoptilometrin, and (±)-Rhodoptilometrin

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The three title compounds have been synthesized and compared with the natural products. Emodin trimethyl ether (11) was brominated and converted into the propenyl derivative (15). The latter could then be transformed into the 3-(2-hydroxypropyl) compound (19) either by oxymercuration–demercuration or by epoxidation and reduction. (±)-Nalgiovensin [1,8-dihydroxy-3-(2-hydroxypropyl)-6-methoxyanthraquinone] (24) was then obtained by partial demethylation. The completely demethylated (±)-isorhodoptilometrin (25) was prepared analogously from the propenylanthraquinone (15) after demethylation and acetylation. For the synthesis of (±)-rhodoptilometrin [1,3,8-trihydroxy-6-(1-hydroxypropyl)anthraquinone] (34), the propenyl derivative (15) was hydrogenated, demethylated, and brominated; substitution of the bromine by acetate and saponification gave the desired product. Conditions for the preparation of the starting material (11) have been further investigated.

AN investigation of the use of keten acetals for the preparation of some naturally occurring anthraquinones [2] has previously led to a relatively simple synthesis of emodin 6,8-dimethyl ether (10), and has now provided the starting material for the synthesis of several hydroxylated propylanthraquinones. In this series only 1,3,8-trihydroxy-6-propylanthraquinone, now recognized as a natural product,[3] and ptilometric acid have been prepared hitherto, as their trimethyl ether [4] and trimethyl ether methyl ester,[5] respectively.

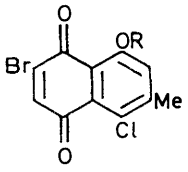
In the original method, 3-bromo-8-chloro-7-methyljuglone (1) reacted with 5 equiv. of keten dimethyl acetal without solvent and gave a 57% yield of the expected anthraquinone (5), which was then dehalogenated (94%). Methylation of the resulting dimethyl ether (10) has now afforded emodin trimethyl ether (11) (96%). On the other hand, when the reaction was attempted with the juglone methyl ether (3), only 6% of the corresponding anthraquinone (7), among other products, could be isolated by chromatography. However, reaction for an extended period afforded a 78% yield of the cyclobutane (4), identified from spectral data. The process is reversible: when the adduct (4) is heated above its m.p. the juglone ether is regenerated. The cyclobutane derivative is surprisingly labile, rearranging at room temperature within 2 days, in chloroform solution, to the known [2] 4-bromo-9-chloro-5-hydroxy-2,6-dimethoxy-8-methylnaphtho[1,2-*b*]furan. Various attempts to convert the adduct (4) into the anthraquinone, in the presence of an excess of keten acetal and with or without acidic or basic catalyst, gave low yields (0—15%), suggesting that the cyclobutane is probably not an intermediate in the reaction.

From the difference in behaviour between the juglone (1) and its methyl ether (3), it appeared that intramolecular acid catalysis was essential for efficient formation of anthraquinones. The fact that the juglone acetate (2), under analogous conditions, produced higher (but unreproducible) yields (14—38%) than the ether (3) (a variable amount of decomposition probably took place during the reaction) also confirmed the need for acid catalysis. Finally if 1 equiv. of acetic acid was added in the reaction of the juglone ether, a yield comparable (54%) to that of the original method was obtained. When acetic acid was replaced by 0.1 equiv. of toluene-*p*-sulphonic acid, four products were isolated including, in 7.5% yield, 4-chloroemodin 1,8-dimethyl ether (8), the occurrence of which is undoubtedly due to acidolysis of an intermediate ketone acetal.

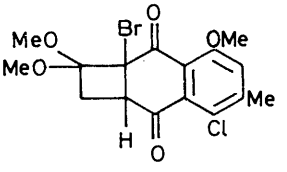
(+)-Nalgiovensin has been obtained from cultures of

[1] Part V, A. Castonguay and P. Brassard, *Synth. Comm.*, 1975, **5**, 377.
[2] J. Banville, J.-L. Grandmaison, G. Lang, and P. Brassard, *Canad. J. Chem.*, 1974, **52**, 80.
[3] G. L. Bartolini, T. R. Erdman, and P. J. Scheuer, *Tetrahedron*, 1973, **29**, 3699.
[4] A. J. Birch and C. J. Moye, *J. Chem. Soc.*, 1961, 4691.
[5] J. K. K. Lam and M. V. Sargent, *J.C.S. Perkin I*, 1974, 1417.

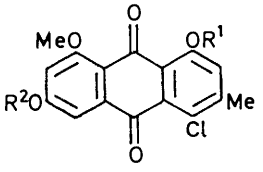
Penicillium nalgiovensis [6] as well as by partial methylation of isorhodoptilometrin,[7] and its structure has been established.[8] For its synthesis the efficiency of various reactions was first explored with the readily accessible pachybasin methyl ether (9). Then emodin 6,8-dimethyl ether (10) was methylated and brominated. The triphenylphosphonium salt of the bromomethyl derivative (13) underwent a Wittig reaction with sodium methoxide and a large excess of acetaldehyde in dimethylformamide



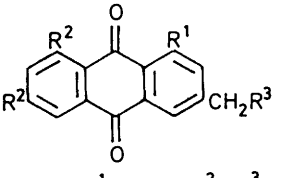
(1) R = H
(2) R = Ac
(3) R = Me



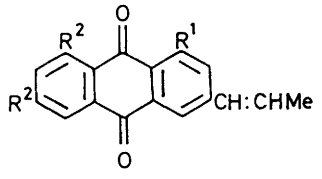
(4)



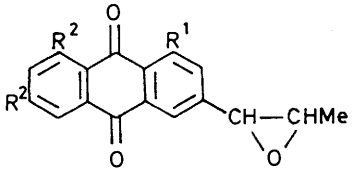
(5) R^1 = H, R^2 = Me
(6) R^1 = Ac, R^2 = Me
(7) R^1 = R^2 = Me
(8) R^1 = Me, R^2 = H



(9) R^1 = OMe, R^2 = R^3 = H
(10) R^1 = OH, R^2 = OMe, R^3 = H
(11) R^1 = R^2 = OMe, R^3 = H
(12) R^1 = OMe, R^2 = H, R^3 = Br
(13) R^1 = R^2 = OMe, R^3 = Br

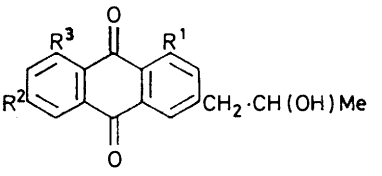


(14) R^1 = OMe, R^2 = H
(15) R^1 = R^2 = OMe
(20) R^1 = R^2 = OH
(21) R^1 = R^2 = OAc

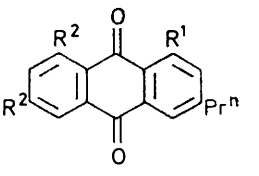


(16) R^1 = OMe, R^2 = H
(17) R^1 = R^2 = OMe
(22) R^1 = R^2 = OAc

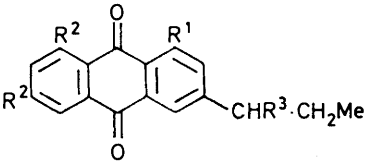
(but not in ethanol), and gave in good yield a 2 : 3 mixture of the *cis*- and *trans*-6-(prop-1-enyl)anthraquinones. The *cis*-compound isomerized during chromatography and the *trans*-material, by acetoxymercuration–demercuration, gave a 35% yield of (±)-isorhodoptilometrin trimethyl ether (19) with the expected orientation.[9,10] On the type of molecule under consideration, mercury(II) acetate and trifluoroacetate alone were ineffective. The reaction requires catalysis by perchloric acid, as prescribed for αβ-unsaturated carbonyl compounds.[10] However lengthy reaction times are needed and this factor is known to have an adverse effect on yields.[9] A longer procedure, giving more easily purified products, consisted of epoxidizing the propenyl compound (15) with *m*-chloroperbenzoic acid and reducing the resulting oxiran (17) by various means of which catalytic hydrogenation over palladium–charcoal was the best. It was difficult to predict the direction of ring opening from the fragmentary published data,[11] but all methods gave the desired product (19). Finally (±)-nalgiovensin (24) was obtained by partial demethylation by anhydrous aluminium chloride in nitrobenzene at 80—90°.



(18) R^1 = OMe, R^2 = R^3 = H
(19) R^1 = R^2 = R^3 = OMe
(23) R^1 = OH, R^2 = R^3 = H
(24) R^1 = R^3 = OH, R^2 = OMe
(25) R^1 = R^2 = R^3 = OH



(26) R^1 = OMe, R^2 = H
(27) R^1 = R^2 = OMe
(28) R^1 = R^2 = OH
(29) R^1 = R^2 = OAc



(30) R^1 = OMe, R^2 = H, R^3 = Br
(31) R^1 = R^2 = OAc, R^3 = Br
(32) R^1 = OMe, R^2 = H, R^3 = OAc
(33) R^1 = OMe, R^2 = H, R^3 = OH
(34) R^1 = R^2 = R^3 = OH

(+)-Isorhodoptilometrin has been isolated from the crinoid *Ptilometra australis* [7] and converted into (+)-nalgiovensin. Since the synthesis of the marine natural product by demethylation of a compound with a hydroxylated side-chain could not be envisaged, this step was carried out on the propenyl derivative (15) by the pyridine hydrochloride method at 160 °C. Acetoxymercuration–demercuration of the triacetate (21) with a large excess of the reagent resulted in extensive decomposition but gave a 12% yield of (±)-isorhodoptilometrin (25). The same reaction applied to the trihydroxy-compound (20) provided only a trace of the desired product. A more satisfactory route consisted as before of converting the acetylated propenyl derivative (21) into the epoxide and reducing the latter.

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[11] G. J. Park and R. Fuchs, *J. Org. Chem.*, 1957, **22**, 93; E. L. Eliel and M. N. Rerick, *J. Amer. Chem. Soc.*, 1960, **82**, 1362; H. C. Brown and Nung Min Yoon, *Chem. Comm.*, 1968, 1549.

Several widely distributed crinoids (*Ptilometra australis*,[7] *Heterometra savignii*,[12] *Lamprometra klunzingeri*,[12] and *Comanthus bennetti* [3]) have yielded the natural pigment (−)-rhodoptilometrin. The possibility of synthesizing this compound by simple hydroboration was first explored with the model propenyl compound (14). Treatment with diborane gave a low yield of the expected [13] mixture of 3-(1-hydroxypropyl) and 3-(2-hydroxypropyl) derivatives after oxidation; 9-borabicyclo[3.3.1]nonane was unreactive. The addition of hydrogen bromide to the trimethoxy-propenylquinone (15) yielded a complex mixture of products; simultaneous demethylation and reduction with hydriodic acid and red phosphorus gave only 12% of the expected compound (28) after reoxidation. Finally the same substrate was catalytically hydrogenated, demethylated with pyridine hydrochloride, and acetylated. The 3-propyl triacetate (29) was then brominated with *N*-bromosuccinimide and converted into the tetra-acetate by heating rapidly with an excess of sodium acetate in dimethylformamide. Saponification of this ester gave (±)-rhodoptilometrin (34).

EXPERIMENTAL

M.p.s were taken for samples in capillary tubes with a Thomas-Hoover apparatus (calibrated thermometer). The i.r. and u.v. spectra were determined with Beckman IR-12 and DK-1A spectrophotometers, respectively. The n.m.r. spectra were recorded with Varian A-60 and Bruker HX-90 spectrometers (tetramethylsilane as internal standard). Davison silica gel No. 923 was used for column chromatography, Baker-7G silica gel for preparative t.l.c. and Woelm silica gel, activity III, for dry column chromatography.

Reactions of 3-Bromo-8-chloro-7-methyljuglone Methyl Ether (3) *with Keten Dimethyl Acetal.*—(a) *Uncatalysed.* A mixture of the ether [2] (3) (316 mg, 1.00 mmol) and the acetal [2,14] (881 mg, 10.0 mmol) was stirred at 100 °C for 1 h, diluted with benzene (5 ml), refluxed for 10 min, diluted again with warm petroleum (b.p. 90—120°; 5 ml), cooled, and filtered to give 8a-*bromo*-4-*chloro*-1,2,2a,8a-*tetrahydro*-1,1,7-*trimethoxy*-5-*methylcyclobuta*[b]*naphthalene*-3,8-*dione* (4) as a white crystalline solid (314 mg, 78%), m.p. 196° (decomp., darkens >150°) [from benzene–petroleum (b.p. 60—110°)]; $\lambda_{max.}$ ($CHCl_3$) 344 nm (log ε 3.76); $\nu_{max.}$ (KBr) 1 707 and 1 687 cm^{-1} (C=O); δ (90 MHz; $CDCl_3$) 2.48 (3 H, s, 5-CH_3), 2.56 (1 H, dd, *J* 9.0 and 13.0 Hz, 2-H), 3.07 (1 H, dd, *J* 2.0 and 13.0 Hz, 2-H), 3.12 (3 H, s, 1-OCH_3), 3.38 (1 H, dd, *J* 2.0 and 9.0 Hz, 2a-H), 3.47 (3 H, s, 1-OCH_3), 3.94 (3 H, s, 7-OCH_3), and 7.11 (1 H, s, 6-H); *m/e* 406/404/402 (M^+) (Found: C, 47.85; H, 3.95. $C_{16}H_{16}BrClO_5$ requires C, 47.6; H, 4.0%).

(b) *Acetic acid-catalysed.* The acetal (450 mg, 5.10 mmol) was added to the ether (3) (316 mg, 1.00 mmol) and acetic acid (60 mg, 1.00 mmol). The suspension was stirred at 120 °C for 2 h, evaporated under vacuum, and chromatographed (dry column; chloroform–ethyl acetate, 19 : 1), and gave 4-chloro-1,6,8-trimethoxy-3-methylanthraquinone (7) (188 mg, 54.4%), m.p. 219° (from ethanol) (lit.,[2] 219.5—220°); *m/e* 348/346 (M^+).

(c) *Toluene-p-sulphonic acid-catalysed.* Toluene-*p*-sulphonic acid (40 mg, 0.21 mmol) was added to the ether (3) (631 mg, 2.00 mmol) and the acetal (881 mg, 1.00 mmol). The mixture was stirred at 115 °C for 40 min, diluted with methanol (5 ml), and cooled. A white precipitate consisted of the cyclobutane (4) (152 mg, 18.8%). The mother liquor was chromatographed (dry column; chloroform–ethyl acetate, 19 : 1) and gave successively 4-chloro-1,6,8-trimethoxy-3-methylanthraquinone (7) (16 mg, 2.3%), m.p. 205—210° (from ethanol) and 4-*chloro*-6-*hydroxy*-1,8-*dimethoxy*-3-*methylanthraquinone* (8) (50 mg, 7.5%), m.p. 294—295° (from chloroform); $\lambda_{max.}$ (EtOH) 221, 268, 280, and 400 nm (log ε 4.48, 4.25, 4.28, and 3.80); $\nu_{max.}$ (KBr) 3 260 (OH), 1 685, and 1 648 cm^{-1} (quinone C=O); δ [90 MHz; $(CD_3)_2SO$] 2.44 (3 H, s, 3-CH_3), 3.85 and 3.89 (2 × 3 H, 2s, 1,8-OCH_3), 6.74 (1 H, d, *J* 2.0 Hz, 7-H), 6.91 (1 H, d, *J* 2.0 Hz, 5-H), and 7.50 (1 H, s, 2-H); *m/e* 332 (M^+) (Found: C, 61.45; H, 3.8. $C_{17}H_{13}ClO_5$ requires C, 61.35; H, 3.95%).

1,3,8-*Trimethoxy*-6-*methylanthraquinone* (11).—A mixture of 1-hydroxy-6,8-dimethoxy-3-methylanthraquinone [2] (10) (3.50 g, 11.7 mmol), dimethyl sulphate (31.0 g, 0.25 mol), anhydrous potassium carbonate (32.0 g, 0.25 mol), and dry acetone (300 ml) was refluxed for 8 h and diluted with water (400 ml). Evaporation of the acetone gave the trimethyl ether (11) (3.45 g, 96%), m.p. 227—228° (from ethanol) (lit.,[15] 225—226°; lit.,[16] 230—232°; lit.,[17] 224—226°; lit.,[18] 163°) (Found: C, 69.15; H, 5.2. $C_{18}H_{16}O_5$ requires C, 69.2; H, 5.15%).

3-*Bromomethyl*-1-*methoxyanthraquinone* (12).—A mixture of 1-methoxy-3-methylanthraquinone [19] (9) (2.00 g, 7.95 mmol), recrystallized *N*-bromosuccinimide (1.55 g, 8.70 mmol), benzoyl peroxide (50 mg), and anhydrous carbon tetrachloride (120 ml) was refluxed for 36 h, cooled, and filtered. The residue, washed with hot water and dried, gave the *bromomethyl compound* (12) (1.35 g, 52%), m.p. 201.5—202.0° (from benzene) (Found: C, 58.05; H, 3.45; Br, 24.25. $C_{16}H_{11}BrO_3$ requires C, 58.0; H, 3.35; Br, 24.15%).

3-*Bromomethyl*-1,6,8-*trimethoxyanthraquinone* (13).—A similar reaction (46 h) between 1,3,8-trimethoxy-6-methylanthraquinone (11) (822 mg, 2.64 mmol) and *N*-bromosuccinimide (565 mg, 3.18 mmol) (the reaction time can be reduced to 1 h by irradiating with a 500 W photoflood lamp) provided the brominated product (13) (973 mg, 75%), m.p. 233.5—234.0° (from benzene); $\lambda_{max.}$ (EtOH) 223, 279, and 398 nm (log ε 4.59, 4.43, and 3.95); $\nu_{max.}$ (KBr) 1 655 cm^{-1} (quinone C=O); δ (90 MHz; $CDCl_3$) 3.91, 3.95, and 4.00 (3 × 3 H, 3s, 1,6,8-OCH_3), 4.51 (2 H, s, 3-CH_2Br), 6.77 (1 H, d, *J* 2.5 Hz, 7-H), 7.30 (1 H, d, *J* 1.8 Hz, 2-H), 7.32 (1 H, d, *J* 2.5 Hz, 5-H), and 7.82 (1 H, d, *J* 1.8 Hz, 4-H); *m/e* 390/392 (M^+). (This compound is unstable and a satisfactory analysis could not be obtained.)

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[17] M. V. Sargent, D. O'N. Smith, and J. A. Elix, *J. Chem. Soc. (C)*, 1970, 307.
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[19] H. Waldmann and P. Sellner, *J. prakt. Chem.*, 1938, **150**, 145.

1-*Methoxy*-3-(trans-*prop*-1-*enyl*)*anthraquinone* (14).—A solution of 3-bromomethyl-1-methoxyanthraquinone (12) (1.075 g, 3.23 mmol) and triphenylphosphine (870 mg, 3.32 mmol) in anhydrous benzene (60 ml) was refluxed for 12 h. The yellow triphenylphosphonium bromide was filtered off, washed with benzene and dry ether, and dried under vacuum (P_2O_5) at 100 °C for 12 h; m.p. 257—258° (decomp.) (1.73 g, 90%). A suspension of this phosphonium salt (1.00 g, 1.68 mmol) in anhydrous dimethylformamide (10 ml) was added to a solution of sodium methoxide (91 mg, 1.68 mmol) in the same solvent (15 ml). The mixture was stirred under nitrogen at room temperature for 5 min and a large excess of redistilled acetaldehyde (15 ml) was added all at once. After 1 h, the mixture was diluted with benzene (200 ml) and washed with water. The residue obtained upon evaporation was chromatographed (column; benzene–ether, 19 : 1) and gave the *propenylquinone* (14) (382 mg, 82%), m.p. 139—140°; δ (90 MHz; $CDCl_3$) 1.93 (3 H, d, $J_{AX} + J_{BX}$ 5.0 Hz, 3′-H_3), 4.03 (3 H, s, 1-OCH_3), 6.49 [2 H, m, AB part of ABX_3, collapsed to dd upon irradiation at δ 1.93, J_{AB} 15.0 Hz, Δν 10.0 Hz, 1′-H(6.43) and 2′-H(6.55)], 7.18 (1 H, d, *J* 1.5 Hz, 2-H), 7.91 (1 H, d, *J* 1.5 Hz, 4-H), and *ca.* 7.6—8.3 (4 H, 2m, 5,6,7,8-H); *m/e* 278 (M^+) (Found: C, 77.65; H, 5.1. $C_{18}H_{14}O_3$ requires C, 77.7; H, 5.05%).

1,3,8-*Trimethoxy*-6-(trans-*prop*-1-*enyl*)*anthraquinone* (15).—A mixture of 3-bromomethyl-1,6,8-trimethoxyanthraquinone (13) (680 mg, 1.74 mmol), triphenylphosphine (506 mg, 1.90 mmol), and anhydrous benzene (50 ml) was refluxed for 32 h. The phosphonium salt was isolated as above (934 mg, 83%); m.p. 225° (decomp.); $\nu_{max.}$ (KBr) 1 666 cm^{-1} (quinone C=O); δ (60 MHz; $CDCl_3$) 3.83 (3 H, s, 6-OCH_3), 3.95 (6 H, s, 1,8-OCH_3), 5.82 (2 H, d, *J* 15.0 Hz, 3-CH_2P), and *ca.* 6.7—8.3 (19 H, m, ArH). The reaction of this phosphonium salt (920 mg, 1.40 mmol) in anhydrous dimethylformamide (20 ml) and sodium methoxide (76 mg, 1.40 mmol) in the same solvent (20 ml) with acetaldehyde (20 ml) was carried out as for compound (14) and gave, after chromatography (column; chloroform–ethyl acetate, 1 : 1), the *quinone* (15) (342 mg, 72%), m.p. 212.0—212.5° (from ethanol); $\lambda_{max.}$ (EtOH) 231, 287, and 430 nm (log ε 4.52, 4.50, and 3.91); $\nu_{max.}$ (KBr) 1 660 cm^{-1} (quinone C=O); δ (90 MHz; $CDCl_3$) 1.90 (3 H, dd, *J* 1.0 and 3.5 Hz, 3′-H_3), 3.90, 3.93, and 3.97 (3 × 3 H, 3s, 1,3,8-OCH_3), 6.22—6.55 (2 H, AB part of ABX_3, J_{AB} 14.0 Hz, 1′- and 2′-H), 6.72 (1 H, d, *J* 2.5 Hz, 2-H), 7.14 (1 H, d, *J* 1.5 Hz, 7-H), 7.28 (1 H, d, *J* 2.5 Hz, 4-H), and 7.75 (1 H, d, *J* 1.5 Hz, 5-H) (Found: C, 70.85; H, 5.55. $C_{20}H_{18}O_5$ requires C, 71.0; H, 5.35%).

3-(1,2-*Epoxypropyl*)-1-*methoxyanthraquinone* (16).—A solution of 1-methoxy-3-(*trans*-prop-1-enyl)anthraquinone (14) (200 mg, 0.72 mmol) and *m*-chloroperbenzoic acid (139 mg, 0.81 mmol) in chloroform (5 ml) was stirred at room temperature for 18 h, diluted with the same solvent (100 ml), and washed successively with aqueous iron(II) sulphate (2.5%), sodium hydrogen carbonate (2.5%), and saturated sodium chloride solutions. Evaporation gave the *oxiran* (16) (160 mg, 76%), m.p. 205.5° (from absolute ethanol) (Found: C, 73.6; H, 4.9. $C_{18}H_{14}O_4$ requires C, 73.45; H, 4.8%).

3-(1,2-*Epoxypropyl*)-1,6,8-*trimethoxyanthraquinone* (17).—A similar reaction (6 h) between 1,3,8-trimethoxy-6-(*trans*-prop-1-enyl)anthraquinone (15) (400 mg, 1.18 mmol) and *m*-chloroperbenzoic acid (250 mg, 1.45 mmol) in chloroform (5 ml) gave the *epoxide* (17) (294 mg, 70%), m.p. 173—174° (from absolute ethanol); $\lambda_{max.}$ (EtOH) 223, 279, and 400 nm (log ε 4.55, 4.33, and 3.76); $\nu_{max.}$ (KBr) 1 660 cm^{-1} (quinone C=O); δ (90 MHz; $CDCl_3$) 1.48 (3 H, d, *J* 5.0 Hz, 3′-H_3), 3.04 (1 H, dq, *J* 2.0 and 5.0 Hz, 2′-H), 3.68 (1 H, d, *J* 2.0 Hz, 1′-H), 3.92, 3.94, and 3.97 (3 × 3 H, 3s, 1,6,8-OCH_3), 6.75 (1 H, d, *J* 2.5 Hz, 7-H), 7.13 (1 H, d, *J* 1.8 Hz, 2-H), 7.30 (1 H, d, *J* 2.5 Hz, 5-H), and 7.74 (1 H, d, *J* 1.8 Hz, 4-H); *m/e* 354 (M^+) (Found: C, 67.6; H, 5.4. $C_{20}H_{18}O_6$ requires C, 67.8; H, 5.1%).

3-(2-*Hydroxypropyl*)-1-*methoxyanthraquinone* (18).—(*a*) Mercury(II) acetate (222 mg, 0.70 mmol) was dissolved in water (1 ml) containing a trace of perchloric acid (5 drops of a 70% solution in 30 ml of water), and tetrahydrofuran (1 ml) was added followed by 1-methoxy-3-(*trans*-prop-1-enyl)anthraquinone (14) (100 mg, 0.360 mmol). The solution was stirred under nitrogen at room temperature for 24 h, then aqueous sodium hydroxide (3N; 2 ml) was added, followed immediately by sodium borohydride (100 mg) in aqueous sodium hydroxide (3N; 2 ml). The mixture was stirred for 1 h, diluted with water (50 ml), and extracted with benzene (3 × 50 ml). The residue obtained upon evaporation of the extract was chromatographed (preparative t.l.c.; chloroform–ethyl acetate 1 : 1) and gave the *hydroxypropyl derivative* (18) (77 mg, 74%), m.p. 145° (from ethanol) (Found: C, 73.1; H, 5.4. $C_{18}H_{16}O_4$ requires C, 72.95; H, 5.45%).

(*b*) To a suspension of lithium aluminium hydride (48 mg, 1.26 mmol) in ether (15 ml) and tetrahydrofuran (5 ml) under nitrogen was added 3-(1,2-epoxypropyl)-1-methoxyanthraquinone (16) (124 mg, 0.423 mmol). The mixture was refluxed for 5 h, hydrolysed with a few drops of water, and evaporated. The residue was taken up in chloroform, washed with water, and chromatographed as in the preceding paragraph to give the same quinone (18) (48 mg, 39%), m.p. 145°.

(*c*) A mixture of 3-(1,2-epoxypropyl)-1-methoxyanthraquinone (16) (236 mg, 0.803 mmol) palladized charcoal (10%; 236 mg) and ethyl acetate (25 ml) was hydrogenated at atmospheric pressure (uptake 2.2 equiv. in 10 min), filtered, left in air for 12 h, and evaporated. The residue was chromatographed (dry column; chloroform–ethyl acetate, 7 : 3) and gave successively 1-methoxy-3-propylanthraquinone (26) (12 mg, 6%) and the hydroxypropyl quinone (18) (163 mg, 69%), m.p. 145°.

3-(2-*Hydroxypropyl*)-1,6,8-*trimethoxyanthraquinone* (19).—(*a*) A similar reaction [section (*a*)] between 1,3,8-trimethoxy-6-(*trans*-prop-1-enyl)anthraquinone (15) (146 mg, 0.430 mmol) and mercury(II) acetate (274 mg, 0.860 mmol) yielded, after chromatography, the quinone (19) (54 mg, 35%), m.p. 189.5—190.0° (from ethanol) (lit.,[6] 187—188°; lit.,[7] 188.5—189.5°) (Found: C, 67.6; H, 5.7. Calc. for $C_{20}H_{20}O_6$: C, 67.4; H, 5.65%).

(*b*) A mixture of 3-(1,2-epoxypropyl)-1,6,8-trimethoxyanthraquinone (17) (220 mg, 0.622 mmol), palladized charcoal (10%; 220 mg), and ethyl acetate (25 ml) was hydrogenated at atmospheric pressure (uptake 2.4 equiv. in 10 min). The filtered solution was left in air for 12 h and evaporated. The residue was chromatographed (dry column; ethyl acetate) and gave the quinone (19) (80 mg, 35%), m.p. 190—191°.

1,3,8-*Trihydroxy*-6-(trans-*prop*-1-*enyl*)*anthraquinone* (20).—A mixture of 1,3,8-trimethoxy-6-(*trans*-prop-1-enyl)-anthraquinone (15) (585 mg, 1.73 mmol) and pyridine hydrochloride (120 g, 1.04 mol) was stirred at 160 °C for 5 h, cooled, and treated with aqueous hydrochloric acid

(1%; 500 ml). The ethyl acetate extract (3 × 200 ml) was washed with water and saturated brine and evaporated. The highly insoluble trihydroxy-quinone (20) (330 mg) could only be purified with difficulty by repeated crystallization from chloroform; m.p. 270—275° (decomp.); $\lambda_{max.}$ (EtOH) 233, 267, 288, 296, 325, and 450 nm (log ε 4.25, 4.14, 4.20, 4.19, 3.82, and 3.91); $\nu_{max.}$ (KBr) 3 190 (OH), 1 650, and 1 616 cm^{-1} (quinone C=O); *m/e* 296 (M^+).

1,3,8-*Triacetoxy*-6-(trans-*prop*-1-*enyl*)*anthraquinone* (21).—A mixture of the crude quinone (20) (330 mg), acetic anhydride (8 ml), and pyridine (4 ml) was stirred at room temperature for 72 h and evaporated under vacuum. The residue was chromatographed (dry column; benzene–ethyl acetate, 9 : 1) and gave the corresponding *triacetate* (21) (259 mg, 35%), m.p. 209—211° (decomp.) [from benzene–petroleum (b.p. 90—120°)]; $\lambda_{max.}$ (EtOH) 211, 261, 277sh, and 342 nm (log ε 4.51, 4.60, 4.25, and 3.73); $\nu_{max.}$ (KBr) 1 774 (ester C=O), 1 678, and 1 660 cm^{-1} (quinone C=O); δ (90 MHz; $CDCl_3$) 1.94 (3 H, d, *J* 5.0 Hz, 3′-H_3), 2.34 (3 H, s, 3-OAc), 2.43 (6 H, s, 1,8-OAc), *ca.* 6.48 (2 H, m, AB part of ABX_3, collapsed to dd upon irradiation at δ 1.94, J_{AB} 16.0 Hz, 1′- and 2′-H), 7.23 (1 H, d, *J* 2.5 Hz, 2-H), 7.29 (1 H, d, *J* 2.0 Hz, 7-H), 7.95 (1 H, d, *J* 2.5 Hz, 4-H), and 8.17 (1 H, d, *J* 2.0 Hz, 5-H); *m/e* 422 (M^+) (Found: C, 65.55; H, 4.2. $C_{23}H_{18}O_8$ requires C, 65.4; H, 4.3%).

1,3,8-*Triacetoxy*-6-(1,2-*epoxypropyl*)*anthraquinone* (22).—A solution of 1,3,8-triacetoxy-6-(*trans*-prop-1-enyl)anthraquinone (21) (150 mg, 0.356 mmol) and *m*-chloroperbenzoic acid (73 mg, 0.426 mmol) in chloroform (treated with silica gel) (3 ml) was stirred at room temperature for 24 h and evaporated under vacuum. The residue was chromatographed (dry column; benzene–ethyl acetate, 9 : 1) and gave the epoxide (22) (107 mg, 68.5%), m.p. 184—185° [from benzene–petroleum (b.p. 60—110°)]; $\lambda_{max.}$ (EtOH) 213, 262, 278sh, and 343 nm (log ε 4.42, 4.53, 4.07, and 3.69); $\nu_{max.}$ (KBr) 1 776 (ester C=O) and 1 672 cm^{-1} (quinone C=O); δ (90 MHz; $CDCl_3$) 1.47 (3 H, d, *J* 5.0 Hz, 3′-H_3), 2.32 (3 H, s, 3-OAc), 2.40 (6 H, s, 1,8-OAc), 3.06 (1 H, m, 2′-H), 3.67 (1 H, d, *J* 2.0 Hz, 1′-H), 7.23 (2 H, m, 2,7-H), 7.93 (1 H, d, *J* 2.5 Hz, 4-H), and 8.09 (1 H, d, *J* 2.0 Hz, 5-H). (This compound is unstable and a satisfactory analysis could not be obtained.)

1-*Hydroxy*-3-(2-*hydroxypropyl*)*anthraquinone* (23).—A mixture of 3-(2-hydroxypropyl)-1-methoxyanthraquinone (18) (124 mg, 0.419 mmol), anhydrous aluminium chloride (5 g), and nitrobenzene (20 ml) was stirred at room temperature for 4 h, poured into cold dilute hydrochloric acid (0.6N; 300 ml), stirred for 1 h, and taken up in benzene (3 × 100 ml). The quinone was extracted with aqueous sodium hydroxide (2N), precipitated with dilute hydrochloric acid, and extracted with chloroform. The residue obtained after evaporation of the extract was chromatographed (preparative t.l.c.; chloroform–ethyl acetate, 1 : 1) and gave the *hydroxypropyl derivative* (23) (104 mg, 88%), m.p. 144.0—144.5° (from ethanol) (Found: C, 72.55; H, 5.0. $C_{17}H_{14}O_4$ requires C, 72.35; H, 5.0%).

1,8-*Dihydroxy*-3-(2-*hydroxypropyl*)-6-*methoxyanthraquinone* [(±)-*Nalgiovensin*] (24).—A similar reaction (3 h) between 3-(2-hydroxypropyl)-1,6,8-trimethoxyanthraquinone (19) (70 mg, 0.196 mmol) and anhydrous aluminium chloride (5 g) in nitrobenzene (50 ml) at 80—90 °C gave, after chromatography (dry column; chloroform–ethyl acetate–methanol, 19 : 19 : 2), a first zone (25 mg; a mixture of dehydrated and partially demethylated products) followed by (±)-*nalgiovensin* (30 mg, 47%), m.p. 194.5° (from ethanol; vacuum sublimation) (lit.,[6] 199—200°; lit.,[7] 196—197°; lit.,[8] 199.5—200.5°); δ (90 MHz; warm $CDCl_3$) 1.28 (3 H, d, *J* 6.0 Hz, 3′-H_3), 2.82 and 2.83 (2 H, 2d, *J* 5.5 and 6.5 Hz, 1′-H_2), 3.94 (3 H, s, 6-OCH_3), 6.67 (1 H, d, *J* 2.5 Hz, 7-H), 7.14br (1 H, s, 2-H), 7.36 (1 H, d, *J* 2.5 Hz, 5-H), 7.66br (1 H, s, 4-H), and 12.07 and 12.23 (2 × 1 H, 2s, 1,8-OH); *m/e* 328 (M^+) and 284 (Found: C, 65.75; H, 4.8. $C_{18}H_{16}O_6$ requires C, 65.85; H, 4.9%). The synthetic compound and the authentic natural product were indistinguishable by t.l.c. in four solvent systems; their mass spectra were superimposable and their i.r. spectra were identical with the exception of minor differences in the 1 250—1 300 cm^{-1} region.

1,3,8-*Trihydroxy*-6-(2-*hydroxypropyl*)*anthraquinone* [(±)-*Isorhodoptilometrin*] (25).—(*a*) A mixture of 1,3,8-triacetoxy-6-(1,2-epoxypropyl)anthraquinone (22) (100 mg, 0.228 mmol), palladized charcoal (10%; 50 mg), and ethyl acetate (8 ml) was hydrogenated at atmospheric pressure (uptake 2.5 equiv. in 15 min). The filtered solution was aerated for 1 h and evaporated. The residue was saponified with aqueous sodium hydroxide (3N; 8 ml) and ethanol (8 ml) at room temperature (3 h), acidified with acetic acid, diluted with water, and extracted with ethyl acetate (3 × 100 ml). The crude product was chromatographed (preparative t.l.c.; chloroform–ethyl acetate–methanol–acetic acid, 30 : 8 : 2 : 1) and yielded successively 1,3,8-trihydroxy-6-propylanthraquinone (28) (10 mg) and (±)-isorhodoptilometrin (32 mg, 45%), m.p. 272.0—272.5° (methanol) (lit.,[7] 275—277°); *m/e* 314 (M^+) and 270 (Found: C, 64.75; H, 4.55. $C_{17}H_{14}O_6$ requires C, 64.95; H, 4.5%). The synthetic material was indistinguishable from a sample of the natural product (i.r. and mass spectra, and t.l.c. in four solvent systems). A reaction (44 h) between 1,3,8-triacetoxy-6-(*trans*-prop-1-enyl)anthraquinone (21) (100 mg, 0.237 mmol) and mercury(II) acetate (302 mg, 0.950 mmol), similar to that used for the preparation of compound (18) [section (*a*)], gave, after chromatography (dry column; chloroform–ethyl acetate–methanol–acetic acid, 30 : 8 : 2 : 1), a first zone consisting of 1,3,8-trihydroxy-6-(*trans*-prop-1-enyl)anthraquinone (20) (14 mg, 20%) and the quinone (25), m.p. 270—271° (9 mg, 12%).

1-*Methoxy*-3-*propylanthraquinone* (26).—A suspension of 1-methoxy-3-(*trans*-prop-1-enyl)anthraquinone (14) (1.60 g, 5.75 mmol) and palladized charcoal (5%; 449 mg) in ethyl acetate (100 ml) was hydrogenated at atmospheric pressure (uptake 2.0 equiv. in 15—20 min). The filtered solution was left for 12 h and evaporated. The residue was chromatographed (dry column; chloroform) and yielded the *propylquinone* (26) (1.337 g, 83%), m.p. 131.5—132.0° (from ethanol); *m/e* 280 (M^+) (Found: C, 77.25; H, 5.6. $C_{18}H_{16}O_3$ requires C, 77.1; H, 5.75%).

1,2,3,4-*Tetrahydro*-5-*methoxy*-7-*propylanthraquinone*.—When the reaction time of the preceding preparation [500 mg of (13), 300 mg of 5% Pd–C and 50 ml of ethyl acetate] was extended to 3.45 h, the uptake of hydrogen was 3 equiv. Chromatography as before gave two incompletely separated products which were isolated by preparative t.l.c. (benzene–ethyl acetate, 9 : 1). A first zone consisted of the *tetrahydro-compound* (211 mg, 42%), m.p. 70.0—70.5° (from ether); $\lambda_{max.}$ (EtOH) 212, 249, 255sh, 275, and 390 nm (log ε 4.59, 4.18, 4.17, 4.16, and 3.62); $\nu_{max.}$ (KBr) 1 655 and 1 632 cm^{-1} (quinone C=O); δ (90 MHz; $CDCl_3$) 0.95 (3 H, t, *J* 7.0 Hz, 3′-H_3), 1.71 (6 H, m, 2′,2,3-H_2), 2.59 (6 H, m, 1′,1,4-H_2), 3.95 (3 H, s, 5-OCH_3), 7.02 (1 H, d,

J 1.5 Hz, 6-H), and 7.41 (1 H, d, *J* 1.5 Hz, 8-H); *m/e* 284 (M^+) (Found: C, 76.25; H, 7.0. $C_{18}H_{20}O_3$ requires C, 76.0; H, 7.1%). A second fraction gave 1-methoxy-3-propylanthraquinone (26) (223 mg, 45%).

1,3,8-*Trimethoxy*-6-*propylanthraquinone* (27).—A suspension of 1,3,8-trimethoxy-6-(*trans*-prop-1-enyl)anthraquinone (15) (433 mg, 1.28 mmol) and palladized charcoal (10%; 300 mg) in ethyl acetate (100 ml) was hydrogenated at atmospheric pressure. After the absorption of 2.0 equiv. of hydrogen, the mixture was filtered, set aside for 12 h, and evaporated. The residue was chromatographed (dry column; chloroform–ethyl acetate, 9 : 1) and gave the quinone (27) (295 mg, 68%), m.p. 167.5—168.5° [from benzene–petroleum (b.p. 60—110°)] (lit.,[4] 169—170°; lit.,[7] 171.0—171.5°); *m/e* 340 (M^+) (Found: C, 70.65; H, 5.8. Calc. for $C_{20}H_{20}O_5$: C, 70.55; H, 5.9%).

1,3,8-*Trihydroxy*-6-*propylanthraquinone* (28).—A mixture of 1,3,8-trimethoxy-6-propylanthraquinone (27) (178 mg, 0.524 mmol) and pyridine hydrochloride (55 g) was stirred at 165 °C for 7 h, cooled, dissolved in hydrochloric acid (2%; 200 ml), and extracted with ethyl acetate (2 × 100 ml). The residue obtained by evaporation of the solvent was chromatographed (dry column; chloroform–ethyl acetate, 9 : 1) and gave the trihydroxylated quinone (28) (140 mg, 89%), m.p. 216.0—216.5° (benzene) (lit.,[3] 219.5—221.5°; lit.,[6] 216.5—217.0; lit.,[7] 216—217°); $\lambda_{max.}$ (EtOH) 222, 253, 266, 290, and 445 nm (log ε 4.38, 4.09, 4.08, 4.15, and 3.92); $\nu_{max.}$ (KBr) 3 390 (OH), 1 670, and 1 620 cm^{-1} (quinone C=O); δ [90 MHz; $(CD_3)_2CO$] 0.97 (3 H, t, *J* 7.0 Hz, 3′-H_3), 1.70 (2 H, m, 2′-H_2), 2.67 (2 H, t, *J* 7.5 Hz, 1′-H_2), 6.57 (1 H, d, *J* 2.5 Hz, 2-H), 7.04 (1 H, d, *J* 1.5 Hz, 7-H), 7.16 (1 H, d, *J* 2.5 Hz, 4-H), and 7.48 (1 H, d, *J* 1.5 Hz, 5-H); *m/e* 298 (M^+) (Found: C, 68.6; H, 4.5. Calc. for $C_{17}H_{14}O_5$: C, 68.45; H, 4.75%).

1,3,8-*Triacetoxy*-6-*propylanthraquinone* (29).—A mixture of 1,3,8-trihydroxy-6-propylanthraquinone (28) (140 mg, 0.470 mmol), acetic anhydride (12 ml), and pyridine (3 ml) was heated at 100 °C for 2.5 h, and evaporated under vacuum. Chromatography (dry column; benzene–ethyl acetate, 9 : 1) of the residue gave the triacetate (29) (179 mg, 90%), m.p. 181.5—182.0° [from benzene–petroleum (b.p. 90—120°)] (lit.,[6] 182—183°) (Found: C, 65.1; H, 4.55. Calc. for $C_{23}H_{20}O_8$: C, 65.1; H, 4.75%).

3-(1-*Bromopropyl*)-1-*methoxyanthraquinone* (30).—A suspension of 1-methoxy-3-propylanthraquinone (26) (400 mg, 1.43 mmol), recrystallized *N*-bromosuccinimide (256 mg, 1.44 mmol), and benzoyl peroxide (50 mg) in dry carbon tetrachloride (20 ml) was refluxed, irradiated with a 500 W photoflood lamp for 0.5 h, filtered, and evaporated. The residue was chromatographed (dry column; benzene–ethyl acetate, 19 : 1) and gave the *bromopropyl derivative* (409 mg, 80%), m.p. 107.5—108.0° [from benzene–petroleum (b.p. 30—80°)]; *m/e* 360/358 (M^+) (Found: C, 60.3; H, 4.1. $C_{18}H_{15}BrO_3$ requires C, 60.2; H, 4.2%).

1,3,8-*Triacetoxy*-6-(1-*bromopropyl*)*anthraquinone* (31).—A similar reaction between 1,3,8-triacetoxy-6-propylanthraquinone (29) (100 mg, 0.236 mmol), *N*-bromosuccinimide (43 mg, 0.240 mmol), and benzoyl peroxide (12 mg), after chromatography (dry column; benzene–ethyl acetate, 24 : 1), gave the *bromopropyl compound* (31) (81 mg, 68%), m.p. 151—152° [from benzene–petroleum (b.p. 60—110°)]; $\lambda_{max.}$ (EtOH) 212, 260, 278sh, and 341 nm (log ε 4.50, 4.59, 4.15, and 3.76); $\nu_{max.}$ (KBr) 1 765 (ester C=O) and 1 675 cm^{-1} (quinone C=O); δ (90 MHz; $CDCl_3$) 1.04 (3 H, t, *J* 7.0 Hz, 3′-H_3), 2.24 (2 H, m, 2′-H_2), 2.33 (3 H, s, 3-OAc), 2.42 (6 H, s, 1,8-OAc), 4.89 (1 H, t, *J* 7.5 Hz, 1′-H), 7.27 (1 H, approx. d, 2-H), 7.45 (1 H, d, *J* 2.0 Hz, 7-H), 7.98 (1 H, d, *J* 2.5 Hz, 4-H), and 8.20 (1 H, d, *J* 2.0 Hz, 5-H); *m/e* 462/460 (*M* − 42) and 382 (Found: C, 55.1; H, 3.6. $C_{23}H_{19}BrO_8$ requires C, 54.9; H, 3.8%).

3-(1-*Acetoxypropyl*)-1-*methoxyanthraquinone* (32).—To fused sodium acetate (380 mg, 4.60 mmol) in anhydrous dimethylformamide (2 ml) at 100 °C was added 3-(1-bromopropyl)-1-methoxyanthraquinone (30) (110 mg, 0.306 mmol) in the same solvent (1 ml). After 7 min, the mixture was cooled, diluted with water, and extracted with benzene. The residue obtained by evaporation of the solvent was chromatographed (dry column; benzene–ethyl acetate, 9 : 1). A first zone consisted of the starting material (6 mg, 5%); a second, of the dehydrohalogenated product (14) (11 mg, 13%). The third fraction gave the *acetate* (33) (72 mg, 70%), m.p. 137.0—137.5° (from ethanol); *m/e* 338 (M^+) (Found: C, 70.9; H, 5.2. $C_{20}H_{18}O_5$ requires C, 71.0; H, 5.35%).

3-(1-*Hydroxypropyl*)-1-*methoxyanthraquinone* (33).—(*a*) A suspension of 3-(1-acetoxypropyl)-1-methoxyanthraquinone (32) (181 mg, 0.535 mmol) in methanol (3 ml) and aqueous sodium hydroxide (3N; 3 ml) was stirred at room temperature for 15 min, then warmed to 80 °C, cooled, diluted with water (100 ml), and extracted with benzene (100 ml). The residue obtained by evaporation of the solvent was chromatographed (dry column; chloroform–ethyl acetate, 9 : 1) and gave the *alcohol* (33) (140 mg, 88.5%), m.p. 132—133° (from methanol); *m/e* 296 (M^+) (Found: C, 72.9; H, 5.4. $C_{18}H_{16}O_4$ requires C, 72.95; H, 5.45%).

(*b*) Solutions of 1-methoxy-3-(*trans*-prop-1-enyl)anthraquinone (14) (181 mg, 0.652 mmol) in anhydrous tetrahydrofuran (3 ml) and of diborane (18 mg, 0.650 mmol) in the same solvent (0.66 ml) were mixed and stirred at 0 °C for 1.5 h, then aqueous sodium hydroxide (3N; 0.2 ml) and hydrogen peroxide (30%; 0.2 ml) were added, After 1 h at room temperature, the mixture was diluted with benzene (100 ml) and washed with water (3 × 100 ml). Evaporation of the organic layer gave a residue which was chromatographed (preparative t.l.c.; chloroform–ethyl acetate, 7 : 3). The two principal zones consisted of 3-(1-hydroxypropyl)-1-methoxyanthraquinone (33) (20 mg, 10.3%) and 3-(2-hydroxypropyl)-1-methoxyanthraquinone (18) (4 mg, 2%).

1,3,8-*Trihydroxy*-6-(1-*hydroxypropyl*)*anthraquinone* [(±)-*Rhodoptilometrin*] (34).—To a solution of fused sodium acetate (270 mg, 3.30 mmol) in anhydrous dimethylformamide (3 ml) at 100 °C was added 1,3,8-triacetoxy-6-(1-bromopropyl)anthraquinone (31) (110 mg, 0.214 mmol) dissolved in the same solvent (2 ml). The resulting solution was stirred at 100 °C for 5 min, cooled, and diluted with ice and water (100 ml). The residue obtained by evaporation of the solvent was saponified with aqueous sodium hydroxide (3N; 3 ml) in ethanol (3 ml) at 60 °C (3 h), diluted with water (100 ml), acidified with dilute hydrochloric acid, and extracted with ethyl acetate (100 ml). Chromatography (preparative t.l.c.; chloroform–ethyl acetate–methanol, 15 : 4 : 1) of the crude product gave a first zone consisting of 1,3,8-trihydroxy-6-(*trans*-prop-1-enyl)anthraquinone (20) (22 mg, 34%). The second fraction yielded (±)-*rhodoptilometrin* (27 mg, 39%), m.p. 216—217° (from methanol–benzene) (lit.,[3] 216—218°; lit.,[7] 217—218°); $\lambda_{max.}$ (EtOH) 222, 250, 266, 290, and 435 nm (log ε 4.46, 4.19, 4.18, 4.22, and 4.01); $\nu_{max.}$ (KBr) 3 350, 1 675, 1 625, 1 565, 1 480, 1 400, 1 335, 1 265, 1 219, 1 170,

1 140, 1 090, 1 025, 1 004, 970, 945, and 915 cm^{-1}; δ [90 MHz; $(CD_3)_2CO$] 0.95 (3 H, t, *J* 7.0 Hz, 3′-H_3), 1.76 (2 H, m, 2′-H_2), 4.73 (1 H, t, *J* 5.5 Hz, 1′-H), 6.60 (1 H, d, *J* 2.0 Hz, 2-H), 7.20 (1 H, d, *J* 2.0 Hz, 4-H), 7.27br (1 H, s, 7-H), 7.72br (1 H, s, 5-H), and 11.41br (2 H, s, 1,8-OH); *m/e* 314 (M^+) and 285 (Found: C, 65.1; H, 4.5. $C_{17}H_{14}O_6$ requires C, 64.95; H, 4.5%). The synthetic compound and the authentic natural product were indistinguishable by t.l.c. in four solvent systems; their mass spectra were identical, as were their i.r. spectra with the exception of minor differences in the 1 350—1 400 cm^{-1} region.

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