The Synthesis of (+)-Coleon A

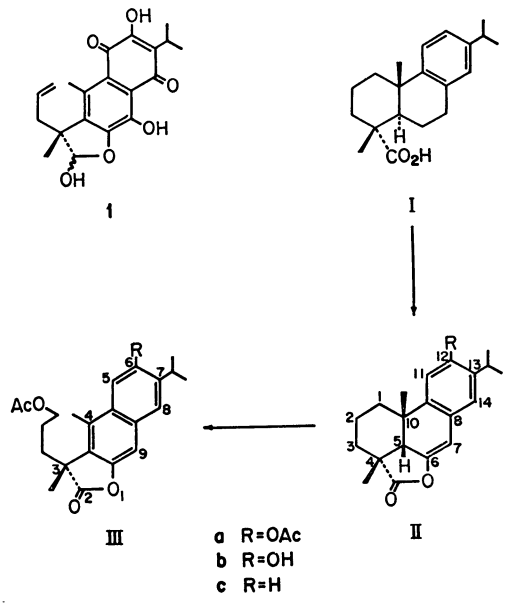
Takashi Matsumoto,* Sachihiko Imai,* Takashi Hirata, Yutaka Fukuda, Tadashi Yamaguchi, and Kazuhiro Inoue

Department of Chemistry, Faculty of Science, Hiroshima University, Higashiseada-machi, Naka-ku, Hiroshima 730

(Received April 14, 1983)

Partial methylation of (*R*)-6-hydroxy-3-(3-hydroxypropyl)-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2(3*H*)-one followed by benzylation afforded the 6-benzyloxy-3-(3-methoxypropyl) derivative, which was converted into the 9-acetyl derivative by the series of reactions; sodium borohydride reduction, acetylation, alkaline hydrolysis, and Jones oxidation. This was oxidized with *m*-chloroperbenzoic acid to give the 9-acetoxy-5,8-quinone derivative, which was further converted into the 5,6,8,9-tetraacetoxy-3-(3-hydroxypropyl) derivative by hydrogenolysis, reductive acetylation, and demethylation. The tetraacetate in pyridine was treated with *o*-nitrophenyl selenocyanate in the presence of tributylphosphine and the resulting selenide was oxidized with hydrogen peroxide to give the 3-allyl derivative. This was converted into (+)-coleon A lactone by alkaline hydrolysis and subsequent oxidation. Finally, (+)-coleon A lactone was reduced with sodium borohydride to give (+)-coleon A which was also obtained by lithium aluminium hydride reduction of the 3-allyl derivative.

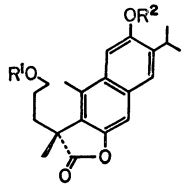
Coleon A (**1**),[1-3] a rare highly oxygenated 1,10-secoabietane derivative, has been isolated from the leaves of *Coleus igniarius* Schweinf. (Labiatae) by Eugster *et al.* In previous papers,[4,5] we have reported the novel conversion of 6-hydroxy-5βH-abieta-6,8,11,13-tetraen-18-oic acid 18,6-lactone derivatives (**IIa—c**) prepared from (+)-dehydroabietic acid (**I**), into the corresponding 1,10-secoabietane derivatives, (*R*)-3-(3-acetoxypropyl)-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]-furan-2(3*H*)-ones (**IIIa—c**). These 1,10-secoabietane derivatives **III** seemed to be useful intermediates for the synthesis of coleon A (**1**). In order to devise an efficient synthetic route for coleon A, some preliminary experiments were carried out on the introduction of oxygen functions into the naphthalene skeleton of **III** and the conversion of an acetoxypropyl side chain into an allyl group. The results were also reported in the preceding paper.[6] As an extension of the previous work, we now describe the synthesis of (+)-coleon A (**1**) starting from (*R*)-6-hydroxy-3-(3-hydroxypropyl)-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2(3*H*)-one (**2**).[6]



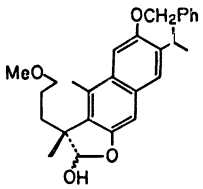
Partial methylation of **2**, prepared from (*R*)-6-acetoxy-3-(3-acetoxypropyl)-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2(3*H*)-one (**IIIa**),[2] with diazomethane and boron trifluoride etherate in ether at room temperature afforded the corresponding 6-hydroxy-3-(3-methoxypropyl) derivative (**3**). This was then converted into (*R*)-6-benzyloxy-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2(3*H*)-one (**4**) by treatment with benzyl chloride and anhydrous potassium carbonate in refluxing *N*,*N*-dimethylformamide. The compound **4** was also obtained from **2** by similar benzylation, followed by methylation of the resulting 6-benzyl ether (**5**). To introduce an acetyl group at C-9,[6] the lactone **4** was reduced with sodium borohydride in ethanol at room temperature and the resulting mixture of C-2 epimeric alcohols (**6**) immediately treated with acetic anhydride in the presence of boron trifluoride etherate at 0—5 °C to give the corresponding 2-acetoxy-9-acetyl derivative (**7**) [IR: 1748 (acetoxyl) and 1679 cm^{-1}(acetyl)]. The structure of **7** was supported by its ^{1}H NMR spectrum which showed singlet signals at δ 2.59 (3H) due to an acetyl and at δ 7.12 (1H) and 8.22 (1H) due to C-5 and C-8 protons. Hydrolysis of the acetoxyl group in **7** with sodium hydrogencarbonate in refluxing aqueous methanol afforded the hemiacetal derivative (**8**), which was oxidized with Jones reagent at 0—5 °C to give (*R*)-9-acetyl-6-benzyloxy-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2(3*H*)-one (**9**: 42% from **IIIa**). The IR spectrum of **9** showed absorption bands at 1803 (γ-lactone) and 1680 cm^{-1}(acetyl). In order to introduce oxygen functions at C-5, C-8, and C-9 in one stage, the acetyl compound **9** in dichloromethane was refluxed with *m*-chloroperbenzoic acid in the presence of *p*-toluenesulfonic acid monohydrate Purification of the crude product gave three *p*-quinone derivatives, **10** (22%), **11** (3%), and **12** (21%). The IR spectrum of **10** showed absorption bands at 1810 (γ-lactone), 1772 (acetoxyl), 1650 cm^{-1} (*p*-quinone), and its ^{1}H NMR spectrum showed signals at δ 1.17 (6H) and 3.27 (1H) due to an isopropyl, at δ 1.63 (3H) and 2.66 (3H) due to two methyls, at δ 2.42

(3H) due to an acetoxyl, at δ 3.20 (3H) due to a methoxyl, and at δ 5.27 (2H) and 7.2—7.5 (5H) due to a benzyl. These spectral data suggested the structure of **10** to be (*R*)-9-acetoxy-6-benzyloxy-2,3,5,8-tetrahydro-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,8-trione. The IR spectra of **11** and **12** showed absorption bands at 1809 (γ-lactone), 1698 (acetyl), 1654 cm^{-1} (*p*-quinone), and at 3360 (hydroxyl), 1820 (γ-lactone), 1712 (acetyl), 1652 cm^{-1} (*p*-quinone), respectively. From these spectral data, the structures of **11** and **12** were assigned respectively to be (*R*)-9-acetyl-6-benzyloxy-2,3,5,8-tetrahydro-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,8-trione and (*R*)-9-acetyl-2,3,5,8-tetrahydro-6-hydroxy-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,8-trione. These structures were further supported by their ^1H NMR spectra (see Experimental section). In order to examine the effect of other substituents at C-6 for the *m*-chloroperbenzoic acid oxidation, the 6-methoxy (**14**) and 6-acetoxy (**15**) derivatives were also prepared as follows. Hydrogenolysis of **9** in acetic acid with 10% Pd–C at 60 °C afforded the corresponding 6-hydroxy compound (**13**); IR: 3590, 3310 br (hydroxyl), 1798 (γ-lactone), 1673 cm^{-1} (acetyl). The compound **13** was converted into **14** (57% from **9**) [IR: 1807 (γ-lactone), 1680 cm^{-1} (acetyl)] and **15** (96% from **9**) [IR: 1811 (γ-lactone), 1762 (acetoxyl), 1688 cm^{-1} (acetyl)] by methylation with methyl iodide and anhydrous potassium carbonate in refluxing acetone and by acetylation with acetic anhydride in pyridine. Oxidation of **14** with *m*-chloroperbenzoic acid and *p*-toluenesulfonic acid monohydrate in refluxing dichloromethane afforded the desired (*R*)-9-acetoxy-2,3,5,8-tetrahydro-7-isopropyl-6-methoxy-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,8-trione (**16**: 11%) [IR: 1808 (γ-lactone), 1768 (acetoxyl), 1652 cm^{-1} (*p*-quinone)] together with its 9-acetyl derivative (**17**: 10%) [IR: 1808 (γ-lactone), 1700 (acetyl), 1657 cm^{-1} (*p*-quinone)]. The similar oxidation of **15** yielded only the Baeyer-Villiger oxidation product, (*R*)-6,9-diacetoxy-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2(3*H*)-one (**18**: 67%) [IR: 1800 (γ-lactone), 1763, 1754 cm^{-1} (acetoxyls)], and no *p*-quinone derivative. The structure of **18** was supported by its ^1H NMR spectrum, which showed singlet signals at δ 2.38 (3H) and 2.47 (3H) due to two acetoxyls, and at δ 7.64 (1H) and 7.75 (1H) due to C-5 and C-8 protons. The above oxidation of **9**, **14**, and **15** indicated that a benzyloxyl group at C-6 increased the yield of the desired acetoxy-*p*-quinone derivative: That is, the benzyloxy derivative **9** was superior to the methoxy (**14**) and acetoxy (**15**) derivatives in one-stage oxidation of C-5, C-8, and C-9. Hydrogenolysis of **10** with 10% Pd-C in acetic acid at 60 °C, followed by reductive acetylation with zinc and acetic anhydride in pyridine at room temperature yielded (*R*)-5,6,8,9-tetraacetoxy-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2(3*H*)-one (**19**: 76%).

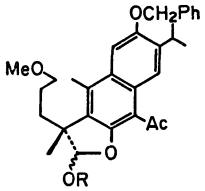
Subsequently, the transformation of a methoxypropyl side chain into an allyl group was carried out as follows. Demethylation[7] of **19** with boron tribromide, sodium iodide, and 15-crown-5 in dichloromethane at



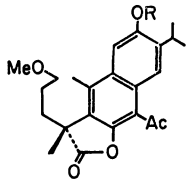
2 $R^1=R^2=H$
3 $R^1=Me$, $R^2=H$
4 $R^1=Me$, $R^2=CH_2Ph$
5 $R^1=H$, $R^2=CH_2Ph$



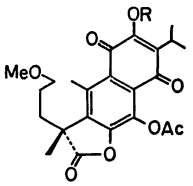
6



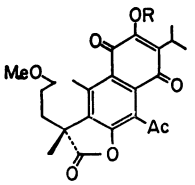
7 R=Ac
8 R=H



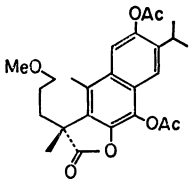
9 $R=CH_2Ph$
13 R=H
14 R=Me
15 R=Ac



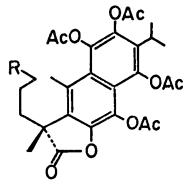
10 $R=CH_2Ph$
16 R=Me



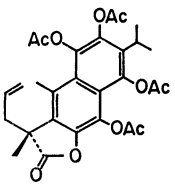
11 $R=CH_2Ph$
12 R=H
17 R=Me



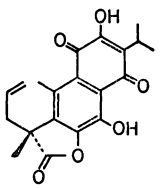
18



19 R=OMe
20 R=OH
21 $R=SeC_6H_4NO_2(o\text{-})$



22



23

—30 °C under a stream of nitrogen afforded the 3-(3-hydroxypropyl) derivative (**20**). This was immediately treated with *o*-nitrophenyl selenocyanate and tributylphosphine in pyridine[8] at room temperature under a stream of nitrogen to give a selenide (**21**: 75% from **19**). Oxidation of **21** with 50% hydrogen peroxide in tetrahydrofuran at room temperature yielded (*R*)-5,6,8,9-tetraacetoxy-3-allyl-7-isopropyl-3,4-dimeth-

ylnaphtho[2,3-*b*]furan-2(3*H*)-one (**22**: 87%), whose ^{1}H NMR spectrum showed signals at δ 2.34 (6H), 2.38 (3H), and 2.39 (3H) due to four acetoxyls and at δ 2.79 (2H) and 4.85—5.6 (3H) due to an allyl. The allyl derivative **22** was then converted into (*R*)-3-allyl-2,3,5,8-tetrahydro-6,9-dihydroxy-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,8-trione (**23**: 40%) [$[\alpha]_D$ +145° (EtOH); IR: 3325 (hydroxyls), 1808 (γ-lactone), 1647 cm^{-1} (*p*-quinone)] by hydrolysis with aqueous potassium hydroxide in refluxing methanol, followed by oxidation with oxygen and subsequent treatment with dilute hydrochloric acid. Reduction of **23** with sodium borohydride in aqueous ethanol afforded a mixture of C-2 epimeric alcohols (**1**: 75%), mp 140.5—141.5 °C, $[\alpha]_D$ +88° ($CHCl_3$); IR: 3580, 3495, 3305 (hydroxyls), 1657 cm^{-1} (*p*-quinone). Compound **1** was also obtained by reduction of **22** with lithium aluminium hydride in refluxing tetrahydrofuran in 34% yield. The physical and spectral data of the synthetic **1** and **23** were in good agreement with those of natural coleon A, mp 136—136.5 °C, $[\alpha]_D$ +80° ($CHCl_3$), and coleon A lactone, $[\alpha]_D$ +144° (EtOH). From the present study, the stetreochemistry of C-3 in coleon A (**1**) was conclusively assigned to be the *R*-configuration, which was previously suggested by Eugster[3,9] on the basis of the incorporation experiments using [2-^{14}C]mevalonic acid.

Experimental

All melting points are uncorrected. The IR spectra and optical rotations were measured in chloroform, and the ^{1}H NMR spectra in deuteriochloroform at 90 MHz, with tetramethylsilane as an internal standard, unless otherwise stated. The chemical shifts are presented in terms of δ values; s: singlet, bs: broad singlet, d: doublet, bd: broad doublet, t: triplet, m: multiplet. The column chromatography was performed using Merck silica gel (0.063 mm).

*(R)-6-Benzyloxy-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-b]furan-2(3H)-one (**4**).* (*R*)-6-Acetoxy-3-(3-acetoxypropyl)-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2(3*H*)-one (**IIIa**)[2] (16.50 g) was hydrolyzed by the known procedure[6] to give the crude (*R*)-6-hydroxy-3-(3-hydroxypropyl)-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2(3*H*)-one (**2**)[6] (13.10 g).

a): To a solution of the above crude **2** (13.10 g) in ether (400 ml) was added successively boron trifluoride etherate (6.40 ml) and a diazomethane ether solution (800 ml), which was prepared from *N*-methyl-*N*-nitrosourea (80 g) by the known procedure and dried over potassium hydroxide. The mixture was allowed to stand at room temperature for 30 min and then filtered to remove resinous material. The filtrate was washed with aqueous sodium hydrogencarbonate and brine, dried over sodium sulfate, and evaporated *in vacuo* to give the crude 6-hydroxy-3-(3-methoxypropyl) derivative (**3**) (13.80 g). IR: 3590, 3300br, 1785, 1620 cm^{-1}; ^{1}H NMR: δ=1.32 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.61 (3H, s, C_3-CH_3), 2.50 (3H, s, C_4-CH_3), 3.22 (3H, s, $-OCH_3$), 3.27 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 3.44 (1H, m, $-C\underline{H}(CH_3)_2$), 6.68 (1H, br, C_6–OH, disappeared with D_2O), 7.23 (2H, s, C_5–H and C_9–H), 7.54 (1H, s, C_8–H).

A mixture of crude **3** (13.80 g), benzyl chloride (5.30 ml), and anhydrous potassium carbonate (58 g) in *N,N*-dimethylformamide (143 ml) was refluxed for 30 min. The mixture was poured into water, acidified with dilute hydrochloric acid, and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo* to give the crude **4** (17.75 g) which was used without purification in the next reaction. The crude **4** obtained from another experiment was purified by column chromatography on silica gel, using ether–benzene (1:9) as the eluent, to give pure **4**. $[\alpha]_D$ +40° (*c* 1.13); IR: 1800, 1645, 1628 cm^{-1}; ^{1}H NMR (CCl_4): δ=1.32 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.58 (3H, s, C_3-CH_3), 2.54 (3H, s, C_4-CH_3), 3.12 (3H, s, $-OCH_3$), 3.13 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 3.47 (1H, m, $-C\underline{H}(CH_3)_2$), 5.18 (2H, s, $-OC\underline{H}_2Ph$), 7.17 (2H, bs, C_5–H and C_9–H), *ca.* 7.2—7.5 (5H, m, $-OCH_2C_6\underline{H}_5$), 7.51 (1H, s, C_8–H). Found: C, 77.64; H, 7.45%. Calcd for $C_{28}H_{32}O_4$: C, 77.75; H, 7.46%.

b): A mixture of the crude **2** (4.00 g) prepared from **IIIa** (4.99 g), benzyl chloride (2.15 ml), anhydrous potassium carbonate (17.0 g), and potassium iodide (2.10 g) in acetone (120 ml) was refluxed for 8 h and then allowed to stand overnight at room temperature. After the mixture had been filtered, the filtrate was evaporated *in vacuo* and the residue was diluted with ether. The ether solution was washed with aqueous sodium thiosulfate and brine, dried over sodium sulfate, and evaporated *in vacuo* to give the crude 6-benzyloxy derivative (**5**) (5.30 g). The crude **5** obtained from another experiment was purified by column chromatography on silica gel, using ether–benzene (1:9) as the eluent, to give pure **5**. $[\alpha]_D$ +41° (*c* 2.24); IR: 3430br, 1797, 1640, 1625 cm^{-1}; ^{1}H NMR: δ=1.35 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.53 (1H, br, –OH, disappeared with D_2O), 1.65 (3H, s, C_3-CH_3), 2.60 (3H, s, C_4-CH_3), 3.47 (2H, t, J=6 Hz, $-C\underline{H}_2OH$), 3.51 (1H, m, $-C\underline{H}(CH_3)_2$), 5.23 (2H, s, $-OC\underline{H}_2Ph$), 7.27 (2H, s, C_5–H and C_9–H), *ca.* 7.30—7.55 (5H, m, $-OCH_2C_6\underline{H}_5$), 7.58 (1H, s, C_8–H). Found: C, 77.76; H, 7.33%. Calcd for $C_{27}H_{30}O_4$: C, 77.48; H, 7.23%.

To a stirred solution of the crude **5** (5.30 g) in ether (290 ml) was added successively boron trifluoride etherate (2.9 ml) and a diazomethane ether solution (250 ml) which was prepared from *N*-methyl-*N*-nitrosourea (25 g) by the known procedure. After work-up as described for the preparation of **3**, crude **4** (5.49 g) was obtained.

*(R)-9-Acetyl-6-benzyloxy-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-b]furan-2(3H)-one (**9**).* *a)*: Sodium borohydride (3.33 g) was added portionwise to a stirred solution of the crude **4** (17.75 g, prepared from **3**) in ethanol (720 ml) with cooling in an ice-water bath. The mixture was stirred at this temperature for 1 h and then at room temperature for 15 h. After the excess hydride had been decomposed with acetone, the mixture was concentrated *in vacuo*, poured into dilute hydrochloric acid, and extracted with chloroform. The chloroform extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo* to give a mixture of the crude C-2 epimeric alcohols (**6**) (16.50 g) which was used without purification in the next reaction. IR: 3610, 3350br, 1628 cm^{-1}; ^{1}H NMR (CCl_4): δ=1.30 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.37 and 1.43 (3H, each s, C_3-CH_3), 2.50 (3H, s, C_4-CH_3), 3.18 and 3.23 (3H, each s, $-OCH_3$), *ca.* 3.1—3.3 (2H, m, $-C\underline{H}_2OMe$), 3.43 (1H, m, $-C\underline{H}(CH_3)_2$), 5.11 (2H, s, $-OC\underline{H}_2Ph$), 5.34 and 5.46 (1H, each s, *ca.* 1:3, C_2–H), 6.82 (1H, s, C_9–H), 7.10 (1H, s, C_5–H), *ca.* 7.2—7.5 (6H, m, C_8–H and $-OCH_2C_6\underline{H}_5$).

Boron trifluoride etherate (16.5 ml) was added to a stirred solution of the crude **6** (16.50 g) in acetic anhydride (330 ml) at 0—5 °C. The mixture was stirred at this temperature for 4 min, poured into a mixture of ice and aqueous sodium hydrogencarbonate, and extracted with chloroform. The chloroform extract was washed with brine, dried over sodium

sulfate, and evaporated *in vacuo* to give a crude epimeric mixture at C-2 of 2-acetoxy-9-acetyl-6-benzyloxy derivative (**7**) (20.00 g) which was used without purification in the next reaction. The crude **7** obtained from another experiment was purified by column chromatography on silica gel, using ether–benzene (8:92) as the eluent, to give pure C-2 epimeric mixture. IR: 1748, 1679 cm^{-1}; ^1H NMR (CCl_4): δ=1.32 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.43 and 1.50 (3H, each s, C_3-CH_3), 1.92 and 2.03 (3H, each s, $-OCOCH_3$), 2.53 (3H, s, C_4-CH_3), 2.59 (3H, s, C_9-COCH_3), 3.17 and 3.23 (3H, each s, $-OCH_3$), *ca.* 3.1—3.3 (2H, m, $-C\underline{H}_2OMe$), 3.45 (1H, m, $-C\underline{H}(CH_3)_2$), 5.16 (2H, s, $-OC\underline{H}_2Ph$), 6.38 and 6.47 (1H, each s, *ca.* 1:3, C_2–H), 7.12 (1H, s, C_5–H), *ca.* 7.2—7.5 (5H, m, $-OCH_2C_6\underline{H}_5$), 8.22 (1H, s, C_8–H). Found: C, 74.28; H, 7.51%. Calcd for $C_{32}H_{38}O_6$: C, 74.10; H, 7.39%.

A mixture of crude **7** (20.00 g) and sodium hydrogencarbonate (17.0 g) in methanol (1600 ml) and water (340 ml) was refluxed for 2 h. The mixture was concentrated *in vacuo* to *ca.* 500 ml, diluted with brine, and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo* to give a crude epimeric mixture at C-2 of 9-acetyl-6-benzyloxy-2-hydroxy derivative (**8**) (17.30 g) which was used without purification in the next reaction. IR: 3610, 3325br, 1668 cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ=1.31 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.28 and 1.37 (3H, each s, C_3-CH_3), 2.47 (3H, s, C_4-CH_3), 2.61 (3H, s, C_9-COCH_3), 3.12 and 3.18 (3H, each s, $-OCH_3$), *ca.* 3.0—3.3 (2H, m, $-C\underline{H}_2OMe$), 3.42 (1H, m, $-C\underline{H}(CH_3)_2$), 5.09 (2H, s, $-OC\underline{H}_2Ph$), *ca.* 5.2—5.5 (2H, m, C_2–H and –OH), 7.05 (1H, s, C_5–H), *ca.* 7.1—7.5 (5H, m, $-OCH_2C_6\underline{H}_5$), 8.13 (1H, s, C_8–H).

Jones reagent [2.5 M (1 M=1 mol dm^{-3}): 28.8 ml] was added dropwise to a stirred solution of crude **8** (17.30 g) in acetone (440 ml) at 0—5 °C. The mixture was stirred at this temperature for 15 min and the excess oxidant decomposed with methanol. The mixture was poured into brine and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (750 g), using ether–benzene (3:97) as the eluent, to give **9** (8.06 g: 42.4% from **IIIa**). This was recrystallized from methanol, mp 140 °C, $[\alpha]_D$ +28° (*c* 0.830); IR: 1803, 1680, 1623 cm^{-1}; ^1H NMR (CCl_4): δ=1.34 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.60 (3H, s, C_3-CH_3), 2.55 (3H, s, C_4-CH_3), 2.70 (3H, s, C_9-COCH_3), 3.12 (3H, s, $-OCH_3$), 3.15 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 3.46 (1H, m, $-C\underline{H}(CH_3)_2$), 5.18 (2H, s, $-OC\underline{H}_2Ph$), 7.17 (1H, s, C_5–H), *ca.* 7.2—7.5 (5H, m, $-OCH_2C_6\underline{H}_5$), 8.16 (1H, s, C_8–H). Found: C, 76.00; H, 7.40%. Calcd for $C_{30}H_{34}O_5$: C, 75.92; H, 7.22%.

b): The crude **4** (5.49 g, prepared from **5**) was also subjected to a series of reactions in *a*) to yield **9** (2.35 g: 40.9% from **IIIa**).

Oxidation of **9** *with* m-*Chloroperbenzoic Acid.* A mixture of **9** (950 mg), *m*-chloroperbenzoic acid (90%: 1550 mg), and *p*-toluenesulfonic acid monohydrate (95 mg) in dichloromethane (47.5 ml) was refluxed for 3 h. The mixture was diluted with ether and the ether solution washed successively with aqueous potassium iodide, aqueous sodium thiosulfate, aqueous sodium hydrogencarbonate, and brine. The dried solution was evaporated *in vacuo*. The residue was chromatographed on silica gel (100 g), using ether–benzene (1:99) as the eluent, to give (*R*)-9-acetoxy-6-benzyloxy-2,3,5,8-tetrahydro-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,8-trione (**10**) (231 mg: 22.2 %). This was recrystallized from methanol, mp 147.5—148.5 °C, $[\alpha]_D$ +32° (*c* 3.32); IR: 1810, 1772, 1650, 1612, 1576 cm^{-1}; ^1H NMR: δ=1.17 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.63 (3H, s, C_3-CH_3), 2.42 (3H, s, $C_9-OCOCH_3$), 2.66 (3H, s, C_4-CH_3), 3.20 (3H, s, $-OCH_3$), 3.23 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 3.27 (1H, m, $-C\underline{H}(CH_3)_2$), 5.27 (2H, s, $-OC\underline{H}_2Ph$), *ca.* 7.2—7.5 (5H, m, $-OCH_2C_6\underline{H}_5$). Found: C, 68.93; H, 6.15%. Calcd for $C_{30}H_{32}O_8$: C, 69.21; H, 6.20%.

Subsequent elution with ether–benzene (3:97) afforded (*R*)-9-acetyl-6-benzyloxy-2,3,5,8-tetrahydro-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,8-trione (**11**) (32 mg: 3.2%), $[\alpha]_D$ +23° (*c* 3.12); IR: 1809, 1698, 1654, 1610, 1568 cm^{-1}; ^1H NMR: δ=1.17 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.62 (3H, s, C_3-CH_3), 2.55 (3H, s, C_9-COCH_3), 2.71 (3H, s, C_4-CH_3), 3.20 (3H, s, $-OCH_3$), 3.23 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 3.29 (1H, m, $-C\underline{H}(CH_3)_2$), 5.32 (2H, s, $-OC\underline{H}_2Ph$), *ca.* 7.25—7.5 (5H, m, $-OCH_2C_6\underline{H}_5$). Found: C, 71.44; H, 6.48%. Calcd for $C_{30}H_{32}O_7$: C, 71.41; H, 6.39%.

Further elution with ether–benzene (1:9) afforded (*R*)-9-acetyl-2,3,5,8-tetrahydro-6-hydroxy-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,8-trione (**12**) (171 mg: 20.6%), $[\alpha]_D$ +26° (*c* 0.35); IR: 3360, 1820, 1712, 1652, 1605, 1580 cm^{-1}; ^1H NMR: δ=1.27 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.62 (3H, s, C_3-CH_3), 2.57 (3H, s, C_9-COCH_3), 2.76 (3H, s, C_4-CH_3), 3.20 (3H, s, $-OCH_3$), 3.24 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 3.30 (1H, m, $-C\underline{H}(CH_3)_2$), 7.79 (1H, bs, C_6–OH, disappeared with D_2O). Found: C, 66.37; H, 6.38%. Calcd for $C_{23}H_{26}O_7$: C, 66.65; H, 6.32%.

*(R)-9-Acetyl-6-hydroxy-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2(3H)-one* (**13**). A mixture of **9** (4.75 g) and 10% Pd–C (1.43 g) in acetic acid (47.5 ml) was submitted to catalytic hydrogenation with 1 atm hydrogen pressure at 60 °C. After the usual work-up, the crude product was chromatographed on silica gel (100 g), using ether–benzene (1:9) as the eluent, to give **13** (3.33 g: 86.5%). This was recrystallized from aqueous methanol, mp 158.5—159.5 °C, $[\alpha]_D$ +19° (*c* 2.42); IR: 3590, 3310br, 1798, 1673, 1615 cm^{-1}; ^1H NMR: δ=1.27 and 1.30 (each 3H, d, and J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.64 (3H, s, C_3-CH_3), 2.47 (3H, s, C_4-CH_3), 2.77 (3H, s, C_9-COCH_3), 3.22 (3H, s, $-OCH_3$), 3.27 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 3.30 (1H, m, $-C\underline{H}(CH_3)_2$), 6.07 (1H, br, –OH, disappeared with D_2O), 7.17 (1H, s, C_5–H), 8.09 (1H, s, C_8–H). Found: C, 71.67; H, 7.37%. Calcd for $C_{23}H_{28}O_5$: C, 71.85; H, 7.34%.

*(R)-9-Acetyl-7-isopropyl-6-methoxy-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2(3H)-one* (**14**). A mixture of **13** (193 mg), methyl iodide (142 mg), and anhydrous potassium carbonate (667 mg) in acetone (4.0 ml) was refluxed for 2 h. The mixture was filtered and the filtrate was evaporated *in vacuo*. The residue was extracted with ether. The ether extract was washed successively with aqueous sodium thiosulfate and brine, dried over sodium sulfate, and evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel (20 g), using ether–benzene (3:97) as the eluent, to give **14** (131 mg: 65.4%). $[\alpha]_D$ +17° (*c* 1.87); IR: 1807, 1680, 1621, 1600 cm^{-1}; ^1H NMR: δ=1.30 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.67 (3H, s, C_3-CH_3), 2.67 (3H, s, C_4-CH_3), 2.77 (3H, s, C_9-COCH_3), 3.21 (3H, s, $-OCH_3$), 3.24 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 3.42 (1H, m, $-C\underline{H}(CH_3)_2$), 3.97 (3H, s, C_6-OCH_3), 7.22 (1H, s, C_5–H), 8.13 (1H, s, C_8–H). Found: C, 72.60; H, 7.64%. Calcd for $C_{24}H_{30}O_5$: C, 72.33; H, 7.59%.

*(R)-6-Acetoxy-9-acetyl-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2(3H)-one* (**15**). The crude phenol **13** (872 mg) prepared from **9** (977 mg) was acetylated with acetic anhydride (4.4 ml) in pyridine (4.4 ml) at room

temperature for 12 h. After the usual work-up, the crude product was chromatographed on silica gel (100 g), using ether–benzene (1:9) as the eluent, to give **15** (844 mg: 96.1% from **9**). $[\alpha]_D$ +16° (*c* 2.88); IR: 1811, 1762, 1688, 1628, 1601 cm^{-1}; ^1H NMR: δ=1.30 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.66 (3H, s, C_3-CH_3), 2.39 (3H, s, $C_6-OCOCH_3$), 2.64 (3H, s, C_4-CH_3), 2.77 (3H, s, C_9-COCH_3), 3.13 (1H, m, $-C\underline{H}(CH_3)_2$), 3.20 (3H, s, $-OCH_3$), 3.23 (3H, t, J=6 Hz, $-C\underline{H}_2OMe$), 7.65 (1H, s, C_5-H), 8.28 (1H, s, C_8-H). Found: C, 70.20; H, 7.37%. Calcd for $C_{25}H_{30}O_6$: C, 70.40; H, 7.09%.

Oxidation of ***14*** *with* m-*Chloroperbenzoic Acid.* A mixture of **14** (1493 mg), *m*-chloroperbenzoic acid (90%: 2250 mg), and *p*-toluenesulfonic acid monohydrate (30 mg) in dichloromethane (75 ml) was refluxed for 3 h. The mixture was diluted with ether and the ether solution washed successively with aqueous potassium iodide, aqueous sodium thiosulfate, aqueous sodium hydrogencarbonate, and brine. The dried solution was evaporated *in vacuo*. The residue was chromatographed on silica gel (150 g), using ether–benzene (2:98) as the eluent, to give (*R*)-9-acetoxy-2,3,5,8-tetrahydro-7-isopropyl-6-methoxy-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,8-trione (**16**) (182 mg: 10.9%). $[\alpha]_D$ +24° (*c* 1.66); IR: 1808, 1768, 1652, 1613 cm^{-1}; ^1H NMR: δ=1.24 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.64 (3H, s, C_3-CH_3), 2.44 (3H, s, $C_9-OCOCH_3$), 2.68 (3H, s, C_4-CH_3), 3.20 (3H, s, $-OCH_3$), 3.24 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 3.29 (1H, m, $-C\underline{H}(CH_3)_2$), 4.00 (3H, s, C_6-OCH_3).

Further elution gave (*R*)-9-acetyl-2,3,5,8-tetrahydro-7-isopropyl-6-methoxy-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,8-trione (**17**) (153 mg: 9.5%), $[\alpha]_D$ +9.2° (*c* 2.18); IR: 1808, 1700, 1657, 1612, 1590, 1567 cm^{-1}; ^1H NMR: δ=1.24 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.62 (3H, s, C_3-CH_3), 2.57 (3H, s, C_9-COCH_3), 2.71 (3H, s, C_4-CH_3), 3.21 (3H, s, $-OCH_3$), 3.24 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 3.31 (1H, m, $-C\underline{H}(CH_3)_2$), 4.05 (3H, s, C_6-OCH_3). Found: C, 66.97; H, 6.37%. Calcd for $C_{24}H_{28}O_7$: C, 67.27; H, 6.59%.

Oxidation of ***15*** *with* m-*Chloroperbenzoic Acid.* A mixture of **15** (954 mg), *m*-chloroperbenzoic acid (90%: 1544 mg), and *p*-toluenesulfonic acid monohydrate (119 mg) in dichloromethane (38 ml) was refluxed for 20 h. After the mixture had been treated as described for the preparation of **16**, the crude product was chromatographed on silica gel (100 g), using ether–benzene (8:92) as the eluent, to give (*R*)-6,9-diacetoxy-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2(3*H*)-one (**18**) (155 mg: 15.7%). $[\alpha]_D$ +21° (*c* 2.15); IR: 1800, 1763, 1754, 1652, 1619 cm^{-1}; ^1H NMR: δ=1.30 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.65 (3H, s, C_3-CH_3), 2.38 and 2.47 (each 3H and s, $C_6-OCOCH_3$ and $C_9-OCOCH_3$), 2.59 (3H, s, C_4-CH_3), 3.14 (1H, m, $-C\underline{H}(CH_3)_2$), 3.18 (3H, s, $-OCH_3$), 3.22 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 7.64 and 7.75 (each 1H and s, C_5-H and C_8-H). Found: C, 68.14; H, 6.92%. Calcd for $C_{25}H_{30}O_7$: C, 67.85; H, 6.83%. Further elution with the same solvent gave a mixture of **18** and the starting **15** (567 mg, *ca.* 9:1 ratio). The total yield of **18** was *ca.* 67%.

*(R)-5,6,8,9-Tetraacetoxy-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2(3H)-one (**19**).* A mixture of **10** (414 mg) and 10% Pd–C (120 mg) in acetic acid (4.2 ml) was submitted to catalytic hydrogenation with 1 atm hydrogen pressure at 60 °C. The crude product, after the usual work-up, was dissolved in acetic anhydride (3.5 ml) and pyridine (3.5 ml) and then zinc powder (130 mg) was added at 0—5 °C. The mixture was stirred at this temperature for 5 min and at room temperature for 1 h, poured into aqueous sodium hydrogencarbonate, and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (50 g), using ether–benzene (2:8) as the eluent, to give **19** (339 mg: 76.3 %). This was recrystallized from methanol, mp 243 °C, $[\alpha]_D$ +13° (*c* 2.80); IR: 1809, 1775, 1648, 1616 cm^{-1}; ^1H NMR: δ=1.26 (6H, bd, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.61 (3H, s, C_3-CH_3), 2.33 and 2.39 (each 6H and s, $C_5-OCOCH_3$, $C_6-OCOCH_3$, $C_8-OCOCH_3$, and $C_9-OCOCH_3$), 2.66 (3H, s, C_4-CH_3), 3.17 (3H, s, $-OCH_3$), 3.21 (3H, m, $-C\underline{H}_2OMe$ and $-C\underline{H}(CH_3)_2$). Found: C, 62.26; H, 6.19%. Calcd for $C_{29}H_{34}O_{11}$: C, 62.36; H, 6.14%.

*(R)-5,6,8,9-Tetraacetoxy-7-isopropyl-3,4-dimethyl-3-[3-(o-nitrophenylselenyl)propyl]naphtho[2,3-*b*]furan-2(3H)-one (**21**).* Boron tribromide dichloromethane solution (1 M: 1.5 ml) was added at −30 °C to a stirred solution of **19** (276 mg) and the 15-crown-5 dichloromethane solution (0.3 M: 9.9 ml) saturated with sodium iodide, under a stream of nitrogen. The mixture was stirred at −30 °C for 3 h. After the addition of aqueous sodium hydrogencarbonate, the mixture was diluted with ether and the ether solution was washed successively with aqueous sodium thiosulfate and brine. The dried solution was evaporated *in vacuo* to give the crude 3-(3-hydroxypropyl) derivative (**20**) which was used without purification in the next reaction. IR: 3530br, 3380br, 1808, 1775, 1648, 1615 cm^{-1}; ^1H NMR: δ=1.26 (6H, bd, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.63 (3H, s, C_3-CH_3), 1.74 (1H, br, –OH, disappeared with D_2O), 2.33 and 2.39 (each 6H and s, $C_5-OCOCH_3$, $C_6-OCOCH_3$, $C_8-OCOCH_3$, and $C_9-OCOCH_3$), 2.67 (3H, s, C_4-CH_3), 3.20 (1H, m, $-C\underline{H}(CH_3)_2$), 3.40 (2H, t, J=6 Hz, $-C\underline{H}_2OH$).

Tributylphosphine (0.53 ml) was added to a stirred mixture of the above crude **20** and *o*-nitrophenyl selenocyanate (457 mg) in pyridine (5.0 ml) at 0—5 °C under a stream of nitrogen. The mixture was stirred at room temperature for 30 min, evaporated *in vacuo*, and diluted with ether. The mixture was filtered to remove a yellow precipitate and the filtrate was evaporated *in vacuo*. The residue was chromatographed on silica gel (60 g), using ether–benzene (1:9) as the eluent, to give **21** (272 mg: 75.5%). IR: 1811, 1778, 1648, 1593, 1510, 1334 cm^{-1}; ^1H NMR: δ=1.27 (6H, bd, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.60 (3H, s, C_3-CH_3), 2.33, 2.34, 2.37, and 2.39 (each 3H and s, $C_5-OCOCH_3$, $C_6-OCOCH_3$, $C_8-OCOCH_3$, and $C_9-OCOCH_3$), 2.53 (3H, bs, C_4-CH_3), *ca.* 2.5—3.0 (2H, m, $-C\underline{H}_2SeC_6H_4-$), 3.20 (1H, m, $-C\underline{H}(CH_3)_2$), *ca.* 7.0—7.3 (3H, m) and *ca.* 8.05—8.3 (1H, m) ($-SeC_6\underline{H}_4-$).

*(R)-5,6,8,9-Tetraacetoxy-3-allyl-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2(3H)-one (**22**).* A mixture of **21** (272 mg) and 50% hydrogen peroxide (0.24 ml) in tetrahydrofuran (8.0 ml) was stirred at room temperature for 17 h. The mixture was diluted with brine and extracted with chloroform. The chloroform extract was washed successively with aqueous potassium iodide, aqueous sodium thiosulfate, aqueous sodium hydrogencarbonate, and brine. The dried solution was evaporated *in vacuo*. The residue was chromatographed on silica gel (20 g), using ether–benzene (1:9) as the eluent, to give **22** (170 mg: 86.5%). This was recrystallized from benzene, mp 269—270 °C, $[\alpha]_D$ +79° (*c* 0.845); IR: 1816, 1780, 1652, 1620, 940 cm^{-1}; ^1H NMR: δ=1.27 (6H, bd, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.64 (3H, s, C_3-CH_3), 2.34 (6H, s), 2.38 (3H, s), and 2.39 (3H, s) ($C_5-OCOCH_3$, $C_6-OCOCH_3$, $C_8-OCOCH_3$, and $C_9-OCOCH_3$), 2.69 (3H, s, C_4-CH_3), 2.79 (2H, bd, J=7 Hz, $-C\underline{H}_2CH=CH_2$), 3.20 (1H, m, $-C\underline{H}(CH_3)_2$), *ca.* 4.85—5.6 (3H, m, $-CH_2C\underline{H}=C\underline{H}_2$). Found: C, 64.17; H, 5.76%.

Calcd for $C_{28}H_{30}O_{10}$: C, 63.87; H, 5.74%.

*(R)-3-Allyl-2,3,5,8-tetrahydro-6,9-dihydroxy-7-isopropyl-3,4-dimethylnaphtho[2,3-b]furan-2,5,8-trione (Coleon A Lactone) (**23**).* A mixture of **22** (200.2 mg) and aqueous potassium hydroxide (10%: 4.5 ml) in methanol (40 ml) was refluxed for 15 min and oxygen was then bubbled into it at room temperature for 30 min. The mixture was acidified with dilute hydrochloric acid, stirred at room temperature for 1 h, and extracted with ether. The ether extract was washed with brine, dried over magnesium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (15 g), using benzene as the eluent, to give **23** (54.7 mg: 40.4 %). $[\alpha]_D$ +145° (EtOH, *c* 0.780); IR: 3325, 1808, 1647, 1617, 928 cm^{-1}; ^1H NMR: δ=1.30 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.65 (3H, s, C_3-CH_3), 2.68 (3H, s, C_4-CH_3), 2.83 (2H, bd, J=6.5 Hz, $-C\underline{H}_2CH=CH_2$), 3.38 (1H, m, $-C\underline{H}(CH_3)_2$), *ca.* 4.87—5.60 (3H, m, $-CH_2C\underline{H}=C\underline{H}_2$), 7.98 (1H, bs, C_6–OH), 13.35 (1H, s, C_9–OH). Found: C, 67.60; H, 5.83%. Calcd for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66%. The spectral data of **23** were in good agreement with those of natural coleon A lactone.

*Coleon A (**1**).* *a)*: A mixture of **23** (50.2 mg), sodium borohydride (33.0 mg), and water (0.4 ml) in ethanol (3.6 ml) was stirred at 0—5 °C for 1 h and then at room temperature for 20 h. The mixture was concentrated *in vacuo*, acidified with dilute hydrochloric acid, and extracted with ether. The ether extract was washed with brine, dried over magnesium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (5.0 g), using ether–benzene (15:85) as the eluent, to give the C-2 epimeric mixture (**1**) (38.1 mg: 75.5%). This was recrystallized from cyclohexane, mp 140.5—141.5 °C, $[\alpha]_D$ +88° (*c* 1.68); IR: 3580, 3495, 3305, 1657, 1612, 918 cm^{-1}; IR (CCl_4): 3505, 3300, 1658, 1614, 918 cm^{-1}; ^1H NMR: δ=1.28 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.44 and 1.50 (3H, each s, *ca.* 0.4:1 ratio, C_3-CH_3), 2.50 (2H, bd, J=6.5 Hz, $-C\underline{H}_2CH=CH_2$), 2.65 (3H, s, C_4-CH_3), 3.34 (1H, m, $-C\underline{H}(CH_3)_2$), *ca.* 4.9—5.25 (2H, m, $-CH_2CH=C\underline{H}_2$), 5.42—5.98 (1H, m, $-CH_2C\underline{H}=CH_2$), 5.78 and 5.90 (1H, each s, C_2–H), 8.13 (1H, s, C_6–OH), 13.48 (1H, s, C_9–OH). Found: C, 67.31; H, 6.32%. Calcd for $C_{20}H_{22}O_6$: C, 67.02; H, 6.19%.

b): A mixture of **22** (170.3 mg) and lithium aluminium hydride (61 mg) in dry tetrahydrofuran (8.0 ml) was refluxed for 2 h. The mixture was poured into ice-dilute hydrochloric acid and extracted with ether. The ether extract was washed with brine, dried over magnesium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (10 g), using ether–benzene (15:85) as the eluent, to give **1** (39.8 mg: 34.3%), whose IR and ^1H NMR spectra were in good agreement with those of natural coleon A.

References

1) C. H. Eugster, H.-P. Küng, H. Kühnis, and P. Karrer, *Helv. Chim. Acta*, **46**, 530 (1963).
2) D. Karanatsios and C. H. Eugster, *Helv. Chim. Acta*, **48**, 471 (1965).
3) C. H. Eugster, *Ber. Deutsch. Bot. Ges.*, **88**, 141 (1975).
4) T. Matsumoto, S. Imai, K. Ondo, N. Takeyama, and K. Fukui, *Chem. Lett.*, **1980**, 425.
5) T. Matsumoto, S. Imai, K. Ondo, N. Takeyama, H. Kataoka, Y. Yamamoto, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **55**, 891 (1982).
6) T. Matsumoto, S. Imai, K. Ondo, H. Kataoka, and K. Kato, *Bull. Chem. Soc. Jpn.*, **56**, 2985 (1983).
7) H. Niwa, T. Hida, and K. Yamada, *Tetrahedron Lett.*, **22**, 4239 (1981).
8) P. A. Grieco, S. Gilman, and M. Nishizawa, *J. Org. Chem.*, **41**, 1485 (1976).
9) Private communication from Professor C. H. Eugster.