Functionalization of (*R*)-3-(3-Acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one and Some Related Compounds

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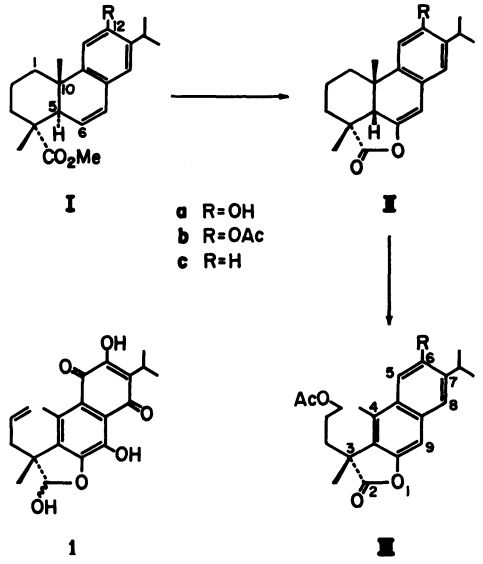
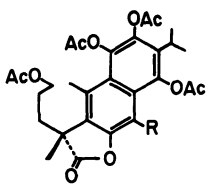
Oxidation of (*R*)-3-(3-acetoxypropyl)-2,3-dihydro-6-hydroxy-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one with Fremy's radical afforded the corresponding *o*-quinone, which was converted into (*R*)-5,6,8-triacetoxy-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one and its 5,6,9-triacetoxy isomer. (*R*)-3-(3-Acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one was also converted into (*R*)-9-acetoxy- and (*R*)-5,8,9-triacetoxy-2,3-dihydro-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]-furan-2-one. Transformation of (*R*)-2,3-dihydro-6-hydroxy-3-(3-hydroxypropyl)-7-isopropyl-3,4-dimethylnaphtho-[2,3-*b*]furan-2-one into (*R*)-6-acetoxy-3-allyl-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one was also achieved.

In previous papers,[1,2] we have reported the conversion of methyl abieta-6,8,11,13-tetraen-18-oate derivatives (**Ia**, **b**, **c**) into (*R*)-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one derivatives (**IIIa**, **b**, **c**) *via* the corresponding 6-hydroxy-5βH-abieta-6,8,11,13-tetraen-18-oic acid 18,6-lactones (**IIa**, **b**, **c**). These naphthalene derivatives (**III**) seem to be useful intermediates for the synthesis of coleon A (**1**),[3,4] a rare highly oxygenated 1,10-secoabietane derivative isolated from the leaves of *Coleus igniarius* Schweinf. (Labiatae) by Eugster *et al.*[5] In order to devise an efficient synthetic route for coleon A, we have now attempted, as a preliminary experiment, to introduce oxygen functions into the naphthalene skeleton of **III** and to transform an acetoxypropyl side chain into an allyl group. This paper describes the syntheses of (*R*)-5,6,8-triacetoxy-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one (**2**) and its 5,6,9-triacetoxy isomer (**3**), and some related compounds, starting from **IIIa**, **b**, **c**.

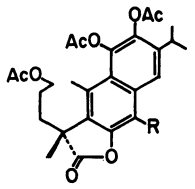
Oxidation of (*R*)-3-(3-acetoxypropyl)-2,3-dihydro-6-hydroxy-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one (**IIIa**)[2] in aqueous acetone with Fremy's radical[6] in the presence of potassium dihydrogenphosphate at room temperature afforded a hydroxy-*p*-quinone (IR: 3355, 1645 cm^{-1}), (*R*)-3-(3-acetoxypropyl)-2,3,5,8-tetrahydro-6-hydroxy-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,8-trione (**4**: 5%), and an *o*-quinone (IR: 1678, 1661 cm^{-1}),[7] (*R*)-3-(3-acetoxypropyl)-2,3,5,6-tetrahydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]-furan-2,5,6-trione (**5**: 40%), together with the starting **IIIa** (22%). The *o*-quinone **5** was then submitted to Thiele-Winter acetoxylation[8] with acetic anhydride and concentrated sulfuric acid at room temperature to give an acetoxy-*p*-quinone (IR: 1775, 1735, 1667 cm^{-1}), (*R*)-6-acetoxy-3-(3-acetoxypropyl)-2,3,5,8-tetrahydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,8-trione (**6**: 7%), and **2** (43%). The *p*-quinones **4** and **6** were each converted into **2** in quantitative yield by reductive acetylation with zinc and acetic anhydride in pyridine at room temperature. Similar treatment of **5** with zinc and acetic anhydride in pyridine afforded (*R*)-5,6-diacetoxy-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one (**7**: 89%). The structure of **2** was supported by its ^{1}H NMR spectrum, which showed a doublet signal due to isopropyl methyls at δ 1.25 (6H) and singlet signals due to two methyls at δ 1.53 and 2.62 (each 3H), four acetoxyls at δ 1.89 (3H), 2.26 (6H), and 2.33 (3H), and an aromatic proton at δ 7.08 (1H). (*R*)-2,3-dihydro-6-hydroxy-3-(3-hydroxypropyl)-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one (**8**), prepared from (*R*)-6-acetoxy-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one (**IIIb**)[2] by hydrolysis with dilute hydrochloric acid in refluxing methanol, was similarly oxidized with Fremy's radical to give the corresponding *o*-quinone (**9**) (IR: 1673, 1658 cm^{-1}), which was converted into **7** (63% from **IIIb**) by reductive acetylation with zinc and acetic anhydride in pyridine. Attempts to introduce an acetyl group at C-9 in **2** and at C-8 or C-9 in **7** by Friedel-Crafts acylation with acetyl chloride and anhydrous aluminium chloride in refluxing carbon disulfide were unsuccessful, giving the starting **2** and **7**. However, nitration of **2** with fuming nitric acid in acetic anhydride at 0 °C and then at room temperature afforded a nitro compound (IR: 1547, 1340 cm^{-1}), (*R*)-5,6,8-triacetoxy-3-(3-acetoxypropyl)-



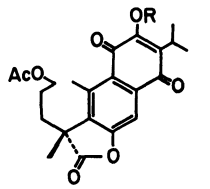
2,3-dihydro-7-isopropyl-3,4-dimethyl-9-nitronaphtho-[2,3-*b*]furan-2-one (**10**: 41%), together with **6** (18%) and an acetoxy-*o*-quinone (IR: 1778, 1735, 1672, 1659 cm^{-1}), (*R*)-8-acetoxy-3-(3-acetoxypropyl)-2,3,5,6-tetrahydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,6-trione (**11**: 17%). Reductive acetylation of **11** with zinc and acetic anhydride in pyridine produced **2** in quantitative yield. For conversion of the nitro group into the hydroxyl group *via* the corresponding amine (**12**), the nitro compound **10** in ethanol was submitted to catalytic hydrogenation over PtO_2 at room temperature under an atmosphere of hydrogen. The IR spectrum of the product (**13**: 51%) showed absorption bands at 1809 (γ-lactone), 1774 and 1736 (acetoxyls), 1660 cm^{-1} (C=N), and no absorption band at 3500—3400 cm^{-1} (NH_2). The ^1H NMR spectrum of **13** showed a doublet signal at δ 1.30 (6H) due to isopropyl methyls and singlet signals at δ 1.56, 1.92, 2.23, 2.24, 2.26, and 2.50 (each 3H) due to three methyls and three acetoxyls. From these spectral data, the structure of **13** was tentatively assigned to be (*R*)-5,6-diacetoxy-8-(3-acetoxypropyl)-8,9-dihydro-4-isopropyl-2,7,8-trimethylfuro-[2′,3′ : 2,3]naphtho[1,8-*de*][1,3]oxazin-9-one. Since the desired amine **12** could not be obtained, the following approach was adopted. Nitration of **7** in acetic anhydride with fuming nitric acid at −10 °C and then at 0—5 °C afforded, in addition to **5** (10%), **6** (4%), and the starting **7** (11%), three nitro compounds **14** (21%) **15** (1%), and **16** (38%). The IR spectrum of **14** showed absorption bands at 1823 (γ-lactone), 1737 (acetoxyl), 1680 and 1658 (*o*-quinone), 1548 and 1309 cm^{-1} (NO_2), and its ^1H NMR spectrum showed a multiplet signal due to an isopropyl methine at very high field (δ 2.66), compared with that (δ 2.98) of **5**. From these spectral data, the structure of **14** was assigned to be (*R*)-3-(3-acetoxypropyl)-2,3,5,6-tetrahydro-7-isopropyl-3,4-dimethyl-8-nitronaphtho[2,3-*b*]furan-2,5,6-trione. The ^1H NMR spectrum of **16** showed signals at δ 1.29 (6H) and 3.02 (1H) due to an isopropyl, at δ 1.63 and 2.70 (each 3H) due to two methyls, at δ 1.91, 2.30, and 2.31 (each 3H) due to three acetoxyls, and at δ 7.74 (1H) due to an aromatic proton. Since the long-range coupling between the isopropyl methine at δ 3.02 and the aromatic proton at δ 7.74 was observed,[9] the structure of **16** was assigned to be (*R*)-5,6-diacetoxy-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethyl-9-nitronaphtho[2,3-*b*]furan-2-one. The IR and ^1H NMR spectra of **15** were very similar to those of **16**, except for a singlet NMR signal at δ 7.02 (1H) due to an aromatic proton. Therefore, both compounds **15** and **16** should be position-isomers with regard to the nitro group. The compound **15** was also obtained by reductive acetylation of **14** with zinc and acetic anhydride in pyridine. Thus, the structure of **15** was assigned to be (*R*)-5,6-diacetoxy-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethyl-8-nitronaphtho[2,3-*b*]furan-2-one. Catalytic hydrogenation of **16** with PtO_2 in acetic acid afforded the corresponding amine (**17**: 80%), which was converted into **3** (20%) and **7** (25%) by successive treatments with sodium nitrite and dilute hydrochloric acid in acetic acid at 0—5 °C, with dilute sulfuric acid at 80 °C, and then with zinc and acetic anhydride in pyridine. The structure of **3** was supported by its ^1H NMR spectrum, which showed signals at δ 1.31 (6H, doublet) and 3.02 (1H, multiplet) due to an isopropyl, at δ 1.64 and 2.66 (each 3H and singlet) due to two methyls, at δ 1.93 (3H), 2.29 (6H), and 2.44 (3H) (each singlet) due to four acetoxyls, and at δ 7.60 (1H, singlet) due to an aromatic proton. Friedel-Crafts acylation of **3** with acetyl chloride and anhydrous aluminium chloride in refluxing carbon disulfide afforded only the starting compound, as in the case of **2**. However nitration of **3** with fuming nitric acid or dilute nitric acid gave a complex mixture. Since functionalization of C-8 in **3** was also unsuccessful, the following experiments were carried out for the introduction of a functional group at C-9 of the naphthalene skeleton.



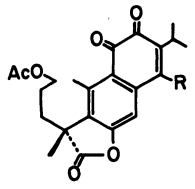
2 R=H
10 R=NO_2
12 R=NH_2



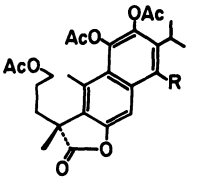
3 R=OAc
16 R=NO_2
17 R=NH_2



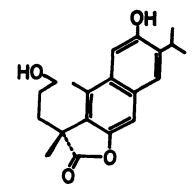
4 R=H
6 R=Ac



5 R=H
11 R=OAc
14 R=NO_2



7 R=H
15 R=NO_2



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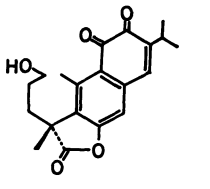

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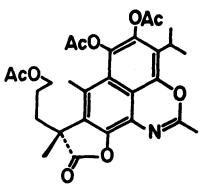

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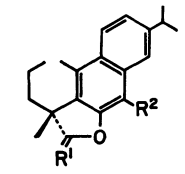
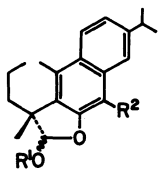
Reduction of (*R*)-2,3-dihydro-7-isopropyl-3,4-dimethyl-3-propylnaphtho[2,3-*b*]furan-2-one (**18**)[2] with lithium aluminium hydride in refluxing ether afforded (*R*)-2,3-dihydro-7-isopropyl-3,4-dimethyl-3-propylna-

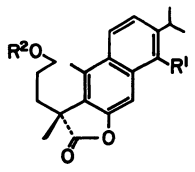
phtho[2,3-*b*]furan (**19**: 29%) and an epimeric mixture at C-2 of 2,3-dihydro-2-hydroxy-7-isopropyl-3,4-dimethyl-3-propylnaphtho[2,3-*b*]furan (**20**: 60%) which gave the corresponding acetate (**21**: 90%) with acetic anhydride in pyridine. The compound **20** was also obtained in quantitative yield by reduction of **18** with sodium borohydride in methanol. Oxidation of **20** with Jones reagent at 0—5 °C gave **18** (93%). Treatment of **21** in acetic anhydride with boron trifluoride etherate at room temperature afforded the corresponding 9-acetyl (**22**: 58%) and 9-acetoacetyl (**23**: 29%) derivatives. Both compounds **22** and **23** were also obtained by the same treatment of **20** in 58% and 20% yields, respectively. The ^{1}H NMR spectrum of **22** showed an acetyl signal at δ 2.58 (3H, singlet) and three aromatic proton signals at δ 7.21 (1H, double doublet, J=2 and 9 Hz), 7.81 (1H, doublet, J=9 Hz), and 8.15 (1H, doublet, J=2 Hz). These chemical shifts and coupling pattern of the aromatic protons suggested the presence of the acetyl group at C-9. The ^{1}H NMR spectrum of **23** also showed similar signals due to three aromatic protons at δ 7.22 (1H, double doublet, J=2 and 9 Hz), 7.82 (1H, doublet, J=9 Hz), and 8.13 (1H, doublet, J=2 Hz), and signals due to an acetoacetyl at δ 2.13 (3H, singlet), 5.93 (1H, singlet), and 15.95 (1H, broad). These spectral data also suggested that the acetoacetyl group was present at C-9 as its enol form. Acetylation of **19** in acetic anhydride with boron trifluoride etherate also gave the corresponding 9-acetyl derivative (**24**: 77%). It is noteworthy that the compounds **19**, **20**, and **21** were each acetylated at C-9 with acetic anhydride and boron trifluoride etherate, because when the lactone **18** was treated in the same manner only the starting material was recovered. In contrast to the above results, acetylation of (*R*)-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one (**IIIc**)[2] with acetyl chloride and anhydrous aluminium chloride in refluxing carbon disulfide afforded the corresponding 8-acetyl derivative (**25**: 54%). The structure of **25** was supported by its ^{1}H NMR spectrum, which showed an acetyl signal at δ 2.54 (3H, singlet) and three aromatic proton signals at δ 7.01 (1H, broad singlet), 7.36 (1H, doublet, J=9 Hz), and 7.91 (1H, doublet, J=9 Hz). Hydrolysis of **IIIc** with concentrated hydrochloric acid in refluxing methanol quantitatively produced the corresponding alcohol (**26**), which was methylated with diazomethane in the presence of boron trifluoride etherate to give (*R*)-2,3-dihydro-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2-one (**27**: 85%). In order to introduce an acetyl group at C-9, the lactone **27** was reduced with sodium borohydride in ethanol and the resulting hemiacetal (**28**) was treated with acetic anhydride and boron trifluoride etherate to give an epimeric mixture at C-2 of 2-acetoxy-9-acetyl-2,3-dihydro-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan (**29**: 70% from **27**). Hydrolysis of **29** with dilute hydrochloric acid in refluxing methanol afforded the corresponding hemiacetal (**30**), which was oxidized with Jones reagent at 0—5 °C to give (*R*)-9-acetyl-2,3-dihydro-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2-one (**31**: 69% from **29**). Treatment of **31** in refluxing dichloromethane with *m*-chloroperbenzoic acid in the presence of *p*-toluenesulfonic acid monohydrate afforded, after column chromatography on silica gel, the corresponding 9-acetoxy derivative (**32**: 11%), together with an acetoxy-*p*-quinone (**33**: 4%) and a mixture of **32** and the starting **31**. The mixture of **31** and **32** was hydrolyzed with dilute hydrochloric acid in refluxing methanol and then purified by column chromatography on silica gel to give **31** (16%) and the 9-hydroxy derivative (**34**: 22% from **31**). Acetylation of **34** with acetic anhydride in pyridine afforded **32** (87%). The structure of **32** was supported by its ^{1}H NMR spectrum, which showed signals due to an acetoxyl at δ 2.45 (3H, singlet) and



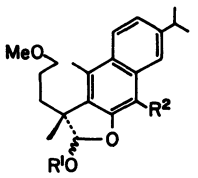
18 R^1=O, R^2=H
19 R^1=H$_2$, R^2=H
24 R^1=H$_2$, R^2=Ac



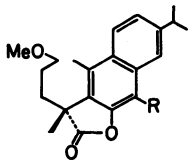
20 R^1=R^2=H
21 R^1=Ac, R^2=H
22 R^1=R^2=Ac
23 R^1=Ac, R^2=COCH=C(OH)Me



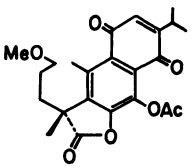
25 R^1=R^2=Ac
26 R^1=R^2=H
27 R^1=H, R^2=Me



28 R^1=R^2=H
29 R^1=R^2=Ac
30 R^1=H, R^2=Ac



31 R=Ac
32 R=OAc
34 R=OH



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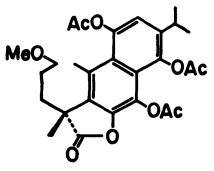
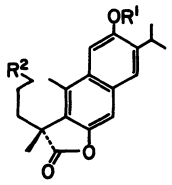
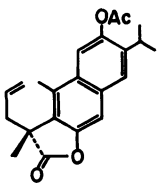


35



36 R^1=H, R^2=SeC$_6$H$_4$NO$_2$(o-)
37 R^1=Ac, R^2=SeC$_6$H$_4$NO$_2$(o-)



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three aromatic protons at δ 7.37 (1H, double doublet, J=2 and 9 Hz), 7.62 (1H, broad singlet), and 7.94 (1H, doublet, J=9 Hz). The IR spectrum of **33** showed absorption bands at 1821 (γ-lactone), 1779 (acetoxyl), 1659 cm^{-1} (p-quinone), and its ^{1}H NMR spectrum showed signals due to an acetoxyl at δ 2.42 (3H, singlet), an olefinic proton at δ 6.55 (1H, doublet, J=1.5 Hz), and no aromatic proton. From these spectral data, the structure of **33** was assigned to be (*R*)-9-acetoxy-2,3,5,8-tetrahydro-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,8-trione. Reductive acetylation of **33** with zinc and acetic anhydride in pyridine afforded the corresponding triacetate (**35**: 45%). It is of interest that the oxygen functions were introduced to C-5, C-8, and C-9 of **31** in one stage by oxidation with *m*-chloroperbenzoic acid, although the yield was low. Therefore if the yield is improved, the 9-acetyl derivatives seem to be useful intermediates for the synthesis of coleon A (**1**).

Finally, transformation of a hydroxypropyl side chain into an allyl group was also carried out as follows. Treatment[10] of **8** with *o*-nitrophenyl selenocyanate and tributylphosphine in pyridine at room temperature under a stream of nitrogen yielded a selenide (**36**), which was immediately acetylated with acetic anhydride in pyridine to give the corresponding 6-acetoxy selenide (**37**: 56% from **8**). Oxidation of **37** with 50% hydrogen peroxide in tetrahydrofuran at room temperature afforded the desired (*R*)-6-acetoxy-3-allyl-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one (**38**: 89%). The structure of **38** was supported by its ^{1}H NMR spectrum, which showed signals due to an acetoxyl at δ 2.32 (3H, singlet), an allyl at δ 2.76 (2H, doublet, J=6.5 Hz) and 4.7—5.6 (3H, multiplet), and three aromatic protons at δ 7.20, 7.50, and 7.58 (each 1H and singlet). Application of the present results for the synthesis of coleon A (**1**) will describe in the succeeding paper.

Experimental

All melting points are uncorrected. The IR spectra and optical rotations were measured in chloroform, and the ^{1}H NMR spectra in carbon tetrachloride 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, dd: double doublet, t: triplet, m: multiplet. The column chromatography was performed using Merck silica gel.

Oxidation of (R)-3-(3-Acetoxypropyl)-2,3-dihydro-6-hydroxy-7-isopropyl-3,4-dimethylnaphtho[2,3-b]furan-2-one (IIIa) with Fremy's Reagent. A solution of freshly prepared Fremy's reagent [potassium nitrosodisulfonate (4.2 g) and aqueous potassium dihydrogenphosphate (0.17 M:† 150 ml) in water (300 ml)] was added to a stirred solution of **IIIa** (1522 mg) in acetone (260 ml) at room temperature. After being stirred for 3 h and then 2 h more, additional Fremy's reagent [potassium nitrosodisulfonate (2.8 g) and aqueous potassium dihydrogenphosphate (0.17 M: 100 ml) in water (200 ml)] was added twice. The mixture was further stirred for 24 h, diluted with 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 (150 g), using ether–benzene (5 : 95) as the eluent, to give (*R*)-3-(3-acetoxypropyl)-2,3,5,8-tetrahydro-6-hydroxy-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,8-trione (**4**) (85 mg: 5.2 %). IR: 3355, 1817, 1732, 1645, 1598, 1585 cm^{-1}; ^{1}H NMR: δ=1.30 (6H, d, J=7 Hz, -CH(C<u>H</u>$_3$)$_2$), 1.61 (3H, s, C$_3$–CH$_3$), 1.94 (3H, s, -OCOCH$_3$), 2.72 (3H, s, C$_4$–CH$_3$), 3.32 (1H, m, -C<u>H</u>(CH$_3$)$_2$), 3.88 (2H, t, J=6.5 Hz, -C<u>H</u>$_2$OAc), 7.70 (1H, s, C$_6$–OH, disappeared with D$_2$O), 7.75 (1H, s, C$_9$–H).

Subsequent elution gave (*R*)-3-(3-acetoxypropyl)-2,3,5,6-tetrahydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,6-trione (**5**) (637 mg: 40.3%). $[\alpha]_D$ +125° (*c* 5.36); IR: 1815, 1735, 1678, 1661, 1598, 1580 cm^{-1}; ^{1}H NMR: δ=1.17 (6H, d, J=7 Hz, -CH(C<u>H</u>$_3$)$_2$), 1.60 (3H, s, C$_3$–CH$_3$), 1.94 (3H, s, -OCOCH$_3$), 2.63 (3H, s, C$_4$–CH$_3$), 2.98 (1H, m, -C<u>H</u>(CH$_3$)$_2$), 3.87 (2H, t, J=6 Hz, -C<u>H</u>$_2$OAc), 6.89 (1H, s, C$_9$–H), 6.99 (1H, bs, C$_8$–H); UV: λ_{max}^{EtOH} 265 nm (log ε 4.38), 358 (3.63). Found: C, 68.56; H, 6.29%. Calcd for C$_{22}$H$_{24}$O$_6$: C, 68.73; H, 6.29%.

Further elution gave the recovered **IIIa** (332 mg: 21.8%).

Thiele-Winter Reaction of 5. Concentrated sulfuric acid (0.08 ml) was added to a stirred solution of **5** (802 mg) in acetic anhydride (8.0 ml) at 0—5 °C. The solution was stirred at room temperature for 4 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 (85 g), using ether–benzene (5 : 95) as the eluent, to give (*R*)-6-acetoxy-3-(3-acetoxypropyl)-2,3,5,8-tetrahydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2,5,8-trione (**6**) (63 mg: 6.8%). $[\alpha]_D$ +10° (*c* 0.77); IR: 1816, 1775, 1735, 1667, 1603, 1588 cm^{-1}; ^{1}H NMR: δ=1.27 (6H, d, J=7 Hz, -CH(C<u>H</u>$_3$)$_2$), 1.61 (3H, s, C$_3$–CH$_3$), 1.93 (3H, s, -CH$_2$-OCOC<u>H</u>$_3$), 2.36 (3H, s, C$_6$–OCOCH$_3$), 2.68 (3H, s, C$_4$–CH$_3$), 3.21 (1H, m, -C<u>H</u>(CH$_3$)$_2$), 3.86 (2H, t, J=6.5 Hz, -C<u>H</u>$_2$OAc), 7.71 (1H, s, C$_9$–H); UV: λ_{max}^{EtOH} 252 nm (log ε 4.31), 353 (3.45). Found: C, 64.91; H, 6.15%. Calcd for C$_{24}$H$_{26}$O$_8$: C, 65.15; H, 5.92%.

Further elution with ether–benzene (15 : 85) afforded (*R*)-5,6,8-triacetoxy-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one (**2**) (478 mg: 43.3%). $[\alpha]_D$ +13° (*c* 1.13); IR: 1807, 1778, 1733, 1641, 1617 cm^{-1}; ^{1}H NMR: δ=1.25 (6H, d, J=7 Hz, -CH(C<u>H</u>$_3$)$_2$), 1.53 (3H, s, C$_3$–CH$_3$), 1.89 (3H, s, -CH$_2$OCOC<u>H</u>$_3$), 2.26 (6H, s) and 2.33 (3H, s) (C$_5$–OCOCH$_3$, C$_6$–OCOCH$_3$, and C$_8$–OCOCH$_3$), 2.62 (3H, s, C$_4$–CH$_3$), 3.10 (1H, m, -C<u>H</u>(CH$_3$)$_2$), 3.77 (2H, t, J=6 Hz, -C<u>H</u>$_2$OAc), 7.08 (1H, s, C$_9$–H); UV: λ_{max}^{EtOH} 241.5 nm (log ε 5.00), 274 (3.81), 285.5 (3.86), 296.5 (3.77), 320.5 (3.17), 335 (3.25). Found: C, 63.91; H, 6.27%. Calcd for C$_{28}$H$_{32}$O$_{10}$: C, 63.62; H, 6.10%.

Reductive Acetylation of 5. Zinc powder (0.1 g) was added to a stirred solution of **5** (470 mg) and acetic anhydride (2.0 ml) in pyridine (2.0 ml) with cooling in an ice–water bath. The mixture was stirred at this temperature for 5 min and then 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 (60 g), using ether–benzene (1 : 9) as the eluent, to give (*R*)-5,6-diacetoxy-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one (**7**) (512 mg: 89.0%). $[\alpha]_D$ +23° (*c* 1.92); IR: 1798, 1769, 1729, 1638 cm^{-1}; ^{1}H NMR: δ=1.30 (6H, d, J=7 Hz, -CH(C<u>H</u>$_3$)$_2$), 1.60 (3H, s, C$_3$–CH$_3$), 1.92 (3H, s, -CH$_2$OCOC<u>H</u>$_3$), 2.28 (6H, s, C$_5$–OCOCH$_3$ and C$_6$–OCOCH$_3$), 2.66 (3H, s, C$_4$–CH$_3$), 2.99 (1H, m, -C<u>H</u>(CH$_3$)$_2$), 3.84 (2H, t, J=6 Hz, -C<u>H</u>$_2$OAc), 7.24 (1H, s, C$_9$–H), 7.50 (1H, s, C$_8$–H); UV: λ_{max}^{EtOH} 239 nm (log ε

† 1 M=1 mol dm^{-3}.

4.94), 272 (3.78), 283 (3.83), 294 (3.71), 318.5 (3.03), 332.5 (3.11). Found: C, 66.29; H, 6.58%. Calcd for $C_{26}H_{30}O_8$: C, 66.37; H, 6.43%.

Nitration of **2**. A solution of fuming nitric acid (d=1.50, 0.62 ml) in acetic anhydride (1.24 ml) was added dropwise over a period of 5 min to a stirred solution of **2** (410 mg) in acetic anhydride (4.1 ml) with cooling in an ice–water bath. The mixture was stirred at room temperature for 30 min, poured into brine, and extracted with ether. The ether extract was washed successively with brine, aqueous sodium hydrogencarbonate, and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (40 g), using ether–benzene (5 : 95) as the eluent, to give a diacetoxy-*p*-quinone (60 mg: 17.5%), whose IR and ^{1}H NMR spectra were identical with those of the authentic **6**.

Subsequent elution gave (*R*)-8-acetoxy-3-(3-acetoxypropyl)-2,3,5,6-tetrahydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]-furan-2,5,6-trione (**11**) (59 mg: 17.2%). $[\alpha]_D$ +45° (c 0.31); IR: 1818, 1778, 1735, 1690, 1672, 1659, 1622, 1600, 1583 cm^{-1}; ^{1}H NMR: δ=1.23 (6H, d, J=7 Hz, -CH(C$\underline{H}_3$)$_2$), 1.59 (3H, s, C_3–CH_3), 1.94 (3H, s, -CH_2OCOC$\underline{H}_3$), 2.44 (3H, s, C_8–OCOCH_3), 2.64 (3H, s, C_4–CH_3), 2.80 (1H, m, -C$\underline{H}$(CH_3)$_2$), 3.86 (2H, t, J=6 Hz, -C$\underline{H}_2$OAc), 6.91 (1H, s, C_9–H); UV: λ_{max}^{EtOH} 241.5 nm (log ε 4.61), 290sh (3.74), 298sh (3.71), 302sh (3.71), 335.5 (3.53). Found: C, 65.45; H, 6.21%. Calcd for $C_{24}H_{26}O_8$: C, 65.15; H, 5.92%.

Further elution with ether–benzene (15 : 85) gave (*R*)-5,6,8-triacetoxy-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethyl-9-nitronaphtho[2,3-*b*]furan-2-one (**10**) 181 mg: (40.7%). This was crystallized from ethanol, mp 171.5—172.5 °C, $[\alpha]_D$ +7° (c 1.04); IR: 1827, 1787, 1737, 1650, 1614, 1547, 1340 cm^{-1}; ^{1}H NMR: δ=1.23 (6H, bd, J=7 Hz, -CH(C$\underline{H}_3$)$_2$), 1.59 (3H, s, C_3–CH_3), 1.92 (3H, s, -CH_2OCOC$\underline{H}_3$), 2.27 (9H, s, C_5–OCOCH_3, C_6–OCOCH_3, and C_8–OCOCH_3), 2.56 (3H, s, C_4–CH_3), 3.00 (1H, m, -C$\underline{H}$(CH_3)$_2$), 3.82 (2H, t, J=6 Hz, -C$\underline{H}_2$OAc). Found: C, 58.88; H, 5.74; N, 2.38%. Calcd for $C_{28}H_{31}O_{12}N$: C, 58.63; H, 5.45; N, 2.44%.

Reductive Acetylation of **4**, **6**, *and* **11**. *a)*: A solution of **4** (80 mg) and acetic anhydride (0.4 ml) in pyridine (0.4 ml) was treated with zinc powder (26 mg) in the same manner as described for the preparation of **7**. The crude product was purified by column chromatography on silica gel (10 g) to give **2** (104 mg: 98%), whose IR and ^{1}H NMR spectra were identical with those of an authentic sample.

b): A solution of **6** (113 mg) and acetic anhydride (0.6 ml) in pyridine (0.6 ml) was treated with zinc powder (33 mg) to give **2** (129 mg: 96%).

c): A solution of **11** (50 mg) and acetic anhydride (0.3 ml) in pyridine (0.3 ml) was treated with zinc powder (15 mg) to give **2** (58 mg: 97%).

*Conversion of (*R*)-6-Acetoxy-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one (**IIIb**) into* **7**. A solution of **IIIb**[2] (4120 mg) and dilute hydrochloric acid (6 M: 83 ml) in methanol (412 ml) was refluxed for 1 h, and then evaporated *in vacuo*. The residue was diluted with brine and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo* to give the crude (*R*)-2,3-dihydro-6-hydroxy-3-(3-hydroxypropyl)-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one (**8**) which, without purification, was used in the next reaction. IR: 3575, 3325br, 1785, 1621 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$): δ=1.33 (6H, d, J=7 Hz, -CH(C$\underline{H}_3$)$_2$), 1.59 (3H, s, C_3–CH_3), 2.50 (3H, s, C_4–CH_3), 3.35 (1H, m, -C$\underline{H}$(CH_3)$_2$), 3.46 (2H, t, J=6 Hz, -C$\underline{H}_2$OH), 6.70 (1H, br, C_6–OH), 7.20 (2H, s, C_5–H and C_9–H), 7.51 (1H, s, C_8–H).

A stirred solution of the above crude **8** in acetone (656 ml) was oxidized with Fremy's reagent [potassium nitrosodisulfonate (13.42 g) and aqueous potassium dihydrogenphosphate (0.17 M: 300 ml) in water (600 ml)] at room temperature. After being stirred for 5 h, additional Fremy's reagent [potassium nitrosodisulfonate (5.36 g) and aqueous potassium dihydrogenphosphate (0.17 M: 120 ml) in water (240 ml)] was added. The mixture was further stirred for 14 h, diluted with brine, and extracted with chloroform. The chloroform extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo* to give the crude (*R*)-2,3,5,6-tetrahydro-3-(3-hydroxypropyl)-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]-furan-2,5,6-trione (**9**) which, without purification, was used in the next reaction. IR: 3580sh, 3490, 3370sh, 1808, 1673, 1658, 1596, 1577 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$): δ=1.19 (6H, d, J=7 Hz, -CH(C$\underline{H}_3$)$_2$), 1.63 (3H, s, C_3–CH_3), 2.68 (3H, s, C_4–CH_3), 3.55 (2H, t, J=6 Hz, -C$\underline{H}_2$OH), 6.99 (1H, s, C_9–H), 7.09 (1H, bs, C_8–H).

Zinc powder (650 mg) was added to a stirred solution of the above crude **9** and acetic anhydride (17 ml) in pyridine (17 ml) at 0—5 °C. After being stirred at 0—5 °C for 5 min and then at room temperature for 1 h, the mixture was filtered and the filtrate was extracted with chloroform. The chloroform extract was washed successively with aqueous sodium hydrogencarbonate and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (220 g), using ether–benzene (5 : 95) as the eluent, to give the starting **IIIb** (640 mg: 15.5%) and **7** (2940 mg: 62.6%). Further elution with ether–benzene (2 : 8) gave **2** (60 mg: 1.1%). The IR and ^{1}H NMR spectra of **2** and **7** were identical with those of authentic samples.

Catalytic Hydrogenation of **10**. A mixture of **10** (57 mg) and PtO_2 (12 mg) in ethanol (5.7 ml) was submitted to catalytic hydrogenation at room temperature for 34 h. After the usual work-up, the crude product was chromatographed on silica gel (5.0 g), using ether–benzene (1 : 3) as the eluent, to give an oxazine derivative (**13**) (27 mg: 51%). IR: 1809, 1774, 1736, 1660, 1623 cm^{-1}; ^{1}H NMR: δ=1.30 (6H, d, J=7 Hz, -CH(C$\underline{H}_3$)$_2$), 1.56 (3H, s, C_3–CH_3), 1.92 (3H, s, -CH_2-OCOC$\underline{H}_3$), 2.23, 2.24, and 2.26 (each 3H and s, C_5–OCOCH_3, C_6–OCOCH_3, and -N=CCH_3), 2.50 (3H, s, C_4–CH_3), 3.04 (1H, m, -C$\underline{H}$(CH_3)$_2$), 3.84 (2H, t, J=6 Hz, -C$\underline{H}_2$OAc).

Nitration of **7**. A solution of fuming nitric acid (d=1.50, 0.94 ml) in acetic anhydride (4.7 ml) was added dropwise to a stirred solution of **7** (2350 mg) in acetic anhydride (35 ml) at −10 °C over a period of 30 min. After being stirred at −10—−5 °C for 1 h and then at 0—5 °C for 50 h, the mixture was poured into aqueous sodium hydrogencarbonate and extracted with chloroform. The extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (260 g), using ether–benzene (5 : 95) as the eluent, to give **6** (85 mg: 3.8%) and (*R*)-3-(3-acetoxypropyl)-2,3,5,6-tetrahydro-7-isopropyl-3,4-dimethyl-8-nitronaphtho[2,3-*b*]furan-2,5,6-trione (**14**) (459 mg: 21.4%). IR: 1823, 1737, 1680, 1658, 1629, 1601, 1583, 1548, 1309 cm^{-1}; ^{1}H NMR: δ=1.29 (6H, d, J=7 Hz, -CH(C$\underline{H}_3$)$_2$), 1.61 (3H, s, C_3–CH_3), 1.92 (3H, s, -CH_2OCOC$\underline{H}_3$), 2.66 (1H, m, -C$\underline{H}$(CH_3)$_2$), 2.67 (3H, s, C_4–CH_3), 3.86 (2H, t, J=6 Hz, -C$\underline{H}_2$OAc), 6.69 (1H, s, C_9–H).

Subsequent elution gave **5** (187 mg: 9.7%), the starting **7** (253 mg: 10.8%), and (*R*)-5,6-diacetoxy-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethyl-8-nitronaphtho[2,3-*b*]-furan-2-one (**15**) (25 mg: 1.0%). This was recrystallized from ether, mp 153—154.5 °C, $[\alpha]_D$ +18° (c 0.55); IR: 1810, 1780, 1732, 1642, 1532, 1331 cm^{-1}; ^{1}H NMR (60 MHz): δ= 1.32 (6H, d, J=7 Hz, -CH(C$\underline{H}_3$)$_2$), 1.58 (3H, s, C_3–CH_3), 1.91 (3H, s, -CH_2OCOC$\underline{H}_3$), 2.33 (6H, s, C_5–OCOCH_3 and C_6–OCOCH_3), 2.70 (3H, s, C_4–CH_3), 3.06 (1H, m, -C$\underline{H}$-(CH_3)$_2$), 3.85 (2H, t, J=6 Hz, -C$\underline{H}_2$OAc), 7.02 (1H, s, C_9–H).

Found: C, 60.54; H, 5.69; N, 2.72%. Calcd for $C_{26}H_{29}O_{10}N$: C, 60.57; H, 5.67; N, 2.72%.

Further elution gave (*R*)-5,6-diacetoxy-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethyl-9-nitronaphtho[2,3-*b*]-furan-2-one (**16**) (970 mg: 37.7%). This was recrystallized from chloroform-carbon tetrachloride, mp 181—182 °C, $[\alpha]_D$ +6° (*c* 0.71); IR: 1820, 1774, 1729, 1642, 1530, 1327 cm^{-1}; ^1H NMR: δ=1.29 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.63 (3H, s, C_3-CH_3), 1.91 (3H, s, $-CH_2OCOC\underline{H}_3$), 2.30 and 2.31 (each 3H and s, $C_5-OCOCH_3$ and $C_6-OCOCH_3$), 2.70 (3H, s, C_4-CH_3), 3.02 (1H, m, $-C\underline{H}(CH_3)_2$), 3.83 (2H, t, J=6 Hz, $-C\underline{H}_2OAc$), 7.74 (1H, s, C_8-H); UV: λ_{max}^{EtOH} 236 nm (log ε 4.86), 265sh (3.98), 322sh (3.47), 335 (3.52). Found: C, 60.86; H, 5.76; N, 2.55%. Calcd for $C_{26}H_{29}O_{10}N$: C, 60.57; H, 5.67; N, 2.72%. The IR and ^1H NMR spectra of **5**, **6**, and **7** were identical with those of authentic samples.

*Reductive Acetylation of **14**.* Zinc powder (17 mg) was added to a stirred solution of **14** (108 mg) and acetic anhydride (0.5 ml) in pyridine (0.5 ml) at 0—5 °C. After being stirred at 0—5 °C for 5 min and then at room temperature for 1 h, the mixture was diluted with ether. The ether solution was washed successively with aqueous sodium hydrogencarbonate, dilute hydrochloric acid, and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (10 g), using ether–benzene (1 : 4) as the eluent, to give **15** (53 mg: 40.9%). The IR and ^1H NMR spectra of **15** were identical with those of an authentic sample.

*(R)-5,6-Diacetoxy-3-(3-acetoxypropyl)-9-amino-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-b]furan-2-one (**17**).* A mixture of **16** (515 mg) and PtO_2 (103 mg) in acetic acid (10 ml) was submitted to catalytic hydrogenation with 1 atm hydrogen pressure at room temperature for 3.5 h. After the usual work-up, the crude product was recrystallized from ethanol to give **17** (388 mg: 80.0%), mp 192.5—193 °C, $[\alpha]_D$ +23° (*c* 0.52); IR: 3440, 3370, 1792, 1770, 1732, 1658, 1625 cm^{-1}; ^1H NMR ($CDCl_3$): δ=1.31 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.62 (3H, s, C_3-CH_3), 1.98 (3H, s, $-CH_2OCOC\underline{H}_3$), 2.36 (6H, s, $C_5-OCOCH_3$ and $C_6-OCOCH_3$), 2.60 (3H, s, C_4-CH_3), 3.07 (1H, m, $-C\underline{H}(CH_3)_2$), *ca.* 3.7—4.3 (2H, br, $-NH_2$), 3.91 (2H, t, J=6 Hz, $-C\underline{H}_2OAc$), 7.62(1H, s, C_8-H). Found: C, 64.01; H, 6.39; N, 2.84%. Calcd for $C_{26}H_{31}O_8N$: C, 64.31; H, 6.44; N, 2.89%.

*(R)-5,6,9-Triacetoxy-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-b]furan-2-one (**3**).* A solution of sodium nitrite (522 mg) in water (10.5 ml) was added dropwise at 0—5 °C to a stirred solution of **17** (1440 mg) and dilute hydrochloric acid (4 M: 18.6 ml) in acetic acid (30 ml). After being stirred at 0—5 °C for 20 min, urea (900 mg) was added. The mixture was stirred for 10 min more, diluted with dilute sulfuric acid (3 M: 500 ml), and then heated at 80 °C for 1 h. After standing overnight at room temperature, the mixture was extracted with chloroform. The extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*.

The above residue was treated with zinc powder (390 mg) and acetic anhydride (6.5 ml) in pyridine (6.5 ml) at room temperature for 1 h. After the same work-up as described for the preparation of **7**, the crude product was chromatographed on silica gel (170 g), using ether–benzene (7 : 93) as the eluent, to give **7** (342 mg: 24.5%) and **3** (315 mg: 20.1%), $[\alpha]_D$ +15° (*c* 2.50); IR: 1802, 1770, 1729, 1653 cm^{-1}; ^1H NMR: δ=1.31 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.64 (3H, s, C_3-CH_3), 1.93 (3H, s, $-CH_2OCOC\underline{H}_3$), 2.29 (6H, s, $C_5-OCOCH_3$ and $C_6-OCOCH_3$), 2.44 (3H, s, $C_9-OCOCH_3$), 2.66 (3H, s, C_4-CH_3), 3.02 (1H, m, $-C\underline{H}(CH_3)_2$), 3.87 (2H, t, J=6 Hz, $-C\underline{H}_2OAc$), 7.60 (1H, s, C_8-H). Found: C, 63.90; H, 6.10%. Calcd for $C_{28}H_{32}O_{10}$: C, 63.62; H, 6.10%.

*Reduction of (R)-2,3-Dihydro-7-isopropyl-3,4-dimethyl-3-propylnaphtho[2,3-b]furan-2-one (**18**) with Lithium Aluminium Hydride.* A mixture of **18**[2] (300 mg) and lithium aluminium hydride (80 mg) in dry ether (12 ml) was refluxed for 4 h with stirring. The mixture was poured into ice-dilute hydrochloric acid 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 hexane–benzene (9 : 1) as the eluent, to give (*R*)-2,3-dihydro-7-isopropyl-3,4-dimethyl-3-propylnaphtho[2,3-*b*]furan (**19**) (84 mg: 29%), $[\alpha]_D$ +28° (*c* 4.02); IR: 1635, 1583 cm^{-1}; ^1H NMR (60 MHz): δ=1.31 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.47 (3H, s, C_3-CH_3), 2.60 (3H, s, C_4-CH_3), 3.00 (1H, m, $-C\underline{H}(CH_3)_2$), 4.14 (2H, ABq, δ_{AB}=14.5 Hz, J_{AB}=8.5 Hz, C_2-H_2), 6.77 (1H, s, C_9-H), 7.05 (1H, dd, J=2 and 9 Hz, C_6-H), 7.31 (1H, d, J=2 Hz, C_8-H), 7.70 (1H, d, J=9 Hz, C_5-H). Found: C, 85.26; H, 9.39%. Calcd for $C_{20}H_{26}O$: C, 85.05; H, 9.28%.

Further elution with ether–benzene (2 : 98) gave an epimeric mixture at C-2 of 2,3-dihydro-2-hydroxy-7-isopropyl-3,4-dimethyl-3-propylnaphtho[2,3-*b*]furan (**20**) (*ca.* 4 : 1 mixture, 180 mg: 59.6%), IR: 3590, 3400br, 1633, 1591 cm^{-1}; ^1H NMR (60 MHz): δ=1.29 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.35 and 1.43 (3H, each s, *ca.* 1: 4, C_3-CH_3), 2.58 (3H, s, C_4-CH_3), 2.99 (1H, m, $-C\underline{H}(CH_3)_2$), 5.39 and 5.48 (1H, each bs, *ca.* 1 : 4, C_2-H), 6.82 (1H, s, C_9-H), 7.09 (1H, dd, J=2 and 8.5 Hz, C_6-H), 7.33 (1H, d, J=2 Hz, C_8-H), 7.71 (1H, d, J=8.5 Hz, C_5-H). Found: C, 80.64; H, 8.81%. Calcd for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78%.

*Reduction of **18** with Sodium Borohydride.* A mixture of **18** (444 mg) and sodium borohydride (114 mg) in methanol (22.2 ml) was stirred at 0—5 °C for 1 h and then allowed to stand overnight at room temperature. The mixture was evaporated *in vacuo*, 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 a product (*ca.* 4 : 1 mixture, 423 mg: 94.6%), whose IR and ^1H NMR spectra were identical with those of authentic **20**.

A stirred solution of **20** (31.4 mg) in acetone (2.0 ml) was oxidized with four drops of Jones reagent (2M) at 0—5 °C for 15 min. The mixture was diluted with water and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo* to give a lactone (29.1 mg: 93.0%), whose IR and ^1H NMR spectra were identical with those of authentic **18**.

A mixture of **20** (182 mg) and acetic anhydride (1.0 ml) in pyridine (0.5 ml) was allowed to stand overnight at room temperature. After the usual work-up, the crude product was chromatographed on silica gel (20 g), using benzene as the eluent, to give an acetate (**21**) (187 mg: 90.1%). IR: 1735, 1633, 1587 cm^{-1}; ^1H NMR (60 MHz): δ=1.30 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.41 and 1.49 (3H, each s, *ca.* 1 : 4, C_3-CH_3), 2.01 (3H, s, $-OCOCH_3$), 2.62 (3H, s, C_4-CH_3), 3.00 (1H, m, $-C\underline{H}(CH_3)_2$), 6.34 and 6.44 (1H, each s, *ca.* 1 : 4, C_2-H), 6.92 (1H, s, C_9-H), 7.14 (1H, dd, J=2 and 8.5 Hz, C_6-H), 7.40 (1H, d, J=2 Hz, C_8-H), 7.78 (1H, d, J=8.5 Hz, C_5-H). Found: C, 77.73; H, 8.31%. Calcd for $C_{22}H_{28}O_3$: C, 77.61; H, 8.29%.

*Acetylation of **19**, **20**, and **21**.* *a)*: Boron trifluoride etherate (0.09 ml) was added to a stirred solution of **19** (84 mg) in acetic anhydride (1.8 ml) with cooling in an ice-water bath. The mixture was stirred at room temperature for 3 min, poured into a mixture of ice and 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 (10 g), using benzene as the eluent, to give (*R*)-9-acetyl-2,3-dihydro-7-isopropyl-3,4-dimethyl-3-propylnaphtho[2,3-*b*]furan(**24**)

(74 mg: 77%), $[\alpha]_D$ +7.3° (*c* 3.01); IR: 1661, 1613, 1585 cm^{-1}; ^1H NMR: δ=1.30 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.45 (3H, s, C_3-CH_3), 2.57 (6H, s, C_4-CH_3 and C_9-COCH_3), 3.00 (1H, m, $-C\underline{H}(CH_3)_2$), 4.24 (2H, ABq, δ_{AB}=22.5 Hz, J_{AB}= 8.5 Hz, C_2-H_2), 7.16 (1H, dd, J=2 and 8.5 Hz, C_6–H), 7.75 (1H, d, J=8.5 Hz, C_5–H), 8.15 (1H, d, J=2 Hz, C_8–H). Found: C, 81.20; H, 8.78%. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70%.

b): A solution of **20** (99.8 mg) in acetic anhydride (2.0 ml) was treated with boron trifluoride etherate (0.1 ml) as described for the preparation of **24**. The crude product was chromatographed on silica gel (20 g), using ether–benzene (2 : 98) as the eluent, to give an epimeric mixture at C-2 of 2-acetoxy-9-acetyl-2,3-dihydro-7-isopropyl-3,4-dimethyl-3-propylnaphtho[2,3-*b*]furan (**22**) (74.0 mg: 57.9%); IR: 1740, 1665, 1613, 1587 cm^{-1}; ^1H NMR: δ=1.31 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.44 and 1.50 (3H, each s, C_3-CH_3), 2.04 and 2.06 (3H, each s, *ca.* 4 : 1, $C_2-OCOCH_3$), 2.58 (3H, s, C_9-COCH_3), 2.63 (3H, s, C_4-CH_3), 3.02 (1H, m, $-C\underline{H}(CH_3)_2$), 6.40 and 6.51 (1H, each s, *ca.* 1 : 4, C_2–H), 7.21 (1H, dd, J=2 and 9 Hz, C_6–H), 7.81 (1H, d, J=9 Hz, C_5–H), 8.15 (1H, d, J=2 Hz, C_8–H). Found: C, 75.22; H, 7.91%. Calcd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91%.

Further elution with ether–benzene (1 : 9) gave an epimeric mixture at C-2 of 9-acetoacetyl-2-acetoxy-2,3-dihydro-7-isopropyl-3,4-dimethyl-3-propylnaphtho[2,3-*b*]furan (**23**) (28.4 mg: 20.0%), whose acetoacetyl group existed only in the enol form. IR: 1737, 1640—1530br cm^{-1}; ^1H NMR: δ=1.30 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.49 (3H, s, C_3-CH_3), 2.05 (3H, s, $-OCOCH_3$), 2.13 (3H, s, $-COCH{=}C(OH)C\underline{H}_3$), 2.63 (3H, s, C_4-CH_3), 3.03 (1H, m, $-C\underline{H}(CH_3)_2$), 5.93 (1H, s, $-COC\underline{H}{=}C(OH)CH_3$), 6.52 (1H, s, C_2–H), 7.22 (1H, dd, J=2 and 9 Hz, C_6–H), 7.82 (1H, d, J=9 Hz, C_5–H), 8.13 (1H, d, J=2 Hz, C_8–H), 15.95 (1H, br, $-COCH{=}C(O\underline{H})CH_3$). Found: C, 73.54; H, 7.69%. Calcd for $C_{26}H_{32}O_5$: C, 73.56; H, 7.60%.

c): A solution of **21** (84.5 mg) in acetic anhydride (1.8 ml) was treated with boron trifluoride etherate (0.09 ml) as described for the preparation of **24**. The crude product was chromatographed on silica gel (10 g) to give **22** (55.0 mg, 57.9%) and **23** (31.0 mg: 29.4%).

(R)-3-(3-Acetoxypropyl)-8-acetyl-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-b]furan-2-one (25). A solution of (*R*)-3-(3-acetoxypropyl)-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]furan-2-one (**IIIc**)[2] (71.0 mg) and acetyl chloride (160 mg) in carbon disulfide (1.4 ml) was added dropwise to a stirred solution of anhydrous aluminium chloride (266 mg) in carbon disulfide (2.7 ml) over a period of 15 min. The mixture was refluxed for 4 h and evaporated *in vacuo*. The residue was decomposed with a mixture of ice and dilute hydrochloric acid, and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel (7.0 g), using ether–benzene (3 : 97) as the eluent, to give **25** (43.0 mg: 54.1%). IR: 1802, 1735, 1697, 1642 cm^{-1}; ^1H NMR: δ=1.30 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.62 (3H, s, C_3-CH_3), 1.92 (3H, s, $-OCOCH_3$), 2.54 (3H, s, $-COCH_3$), 2.64 (3H, s, C_4-CH_3), 2.94 (1H, m, $-C\underline{H}(CH_3)_2$), 3.86 (2H, t, J=6.5 Hz, $-C\underline{H}_2OAc$), 7.01 (1H, bs, C_9–H), 7.36 (1H, d, J=9 Hz, C_6–H), 7.91 (1H, d, J=9 Hz, C_5–H). Found: C, 72.98; H, 7.16%. Calcd for $C_{24}H_{28}O_5$: C, 72.70; H, 7.12%.

(R)-2,3-Dihydro-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-b]furan-2-one (27). The diazomethane ether solution (600 ml) was prepared from *N*-methyl-*N*-nitrosourea (60 g) by the known procedure and it was then dried over potassium hydroxide. To a stirred solution of (*R*)-2,3-dihydro-3-(3-hydroxypropyl)-7-isopropyl-3,4-dimethylnaphtho[2,3-*b*]-furan-2-one (**26**)[2] (9.94 g) in ether (500 ml) was added successively boron trifluoride etherate (1.9 ml) and the above diazomethane ether solution (600 ml). The mixture was allowed to stand at room temperature for 30 min and then filtered to remove a resinous material. The filtrate was washed successively with aqueous sodium hydrogencarbonate and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (300 g), using benzene as the eluent, to give **27** (8.87 g: 85.4%). $[\alpha]_D$ +27° (*c* 1.71); IR: 1792, 1637, 1592 cm^{-1}; ^1H NMR: δ=1.32 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.59 (3H, s, C_3-CH_3), 2.62 (3H, s, C_4-CH_3), 3.01 (1H, m, $-C\underline{H}(CH_3)_2$), 3.12 (3H, s, $-OCH_3$), 3.13 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 7.18 (1H, s, C_9–H), 7.24 (1H, dd, J=2 and 8.5 Hz, C_6–H), 7.48 (1H, d, J=2 Hz, C_8–H), 7.82 (1H, d, J=8.5 Hz, C_5–H). Found: C, 77.28; H, 7.97%. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03%.

(3R)-2ξ-Acetoxy-9-acetyl-2,3-dihydro-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-b]furan (29). A mixture of **27** (699 mg) and sodium borohydride (163 mg) in ethanol (35 ml) was stirred at room temperature for 20 h. The mixture was evaporated *in vacuo*, 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 an epimeric mixture at C-2 of the corresponding alcohol (**28**) (713 mg) which, without purification, was used in the next reaction. IR: 3600, 3350br, 1635, 1593 cm^{-1}; ^1H NMR (60 MHz): δ=1.31 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.37 and 1.44 (3H, each s, C_3-CH_3), 2.59 (3H, s, C_4-CH_3), 2.99 (1H, m, $-C\underline{H}(CH_3)_2$), 3.19 and 3.26 (3H, each s, $-OCH_3$), *ca.* 3.1—3.4 (2H, m, $-C\underline{H}_2OMe$), 4.1 (1H, br, –OH), 5.37 and 5.50 (1H, each bs, *ca.* 1 : 3, C_2–H), 6.84 (1H, s, C_9–H), 7.11 (1H, bd, J=9 Hz, C_6–H), 7.36 (1H, bs, C_8–H), 7.76 (1H, d, J=9 Hz, C_5–H).

Boron trifluoride etherate (0.71 ml) was added to a stirred solution of the above crude **28** (713 mg) in acetic anhydride (14.2 ml) at 0—5 °C. The mixture was stirred at this temperature for 4 min and then treated as described for the preparation of **24**. The crude product was chromatographed on silica gel (90 g), using ether–benzene (5 : 95) as the eluent, to give **29** (618 mg: 70.0% from **27**). IR: 1748, 1675, 1621, 1597 cm^{-1}; ^1H NMR (60 MHz): δ=1.30 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.45 and 1.52 (3H, each s, C_3-CH_3), 2.04 and 2.07 (3H, each s, $C_2-OCOCH_3$), 2.60 (3H, s, C_9-COCH_3), 2.64 (3H, s, C_4-CH_3), 3.02 (1H, m, $-C\underline{H}(CH_3)_2$), 3.17 and 3.24 (3H, each s, $-OCH_3$), *ca.* 3.1—3.4 (2H, m, $-C\underline{H}_2OMe$), 6.40 and 6.50 (1H, each s, *ca.* 1 : 3, C_2–H), 7.20 (1H, dd, J= 2.5 and 9 Hz, C_6–H), 7.77 (1H, d, J=9 Hz, C_5–H), 8.11 (1H, d, J=2.5 Hz, C_8–H). Found: C, 72.62; H, 7.83%. Calcd for $C_{25}H_{32}O_5$: C, 72.79; H, 7.82%.

(R)-9-Acetyl-2,3-dihydro-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-b]furan-2-one (31). A mixture of **29** (484 mg) and dilute hydrochloric acid (6M: 0.6 ml) in methanol (20 ml) was refluxed for 1 h. The mixture was evaporated *in vacuo* and extracted with ether. The ether extract was washed successively with aqueous sodium hydrogencarbonate and brine, dried over sodium sulfate, and evaporated *in vacuo* to give an epimeric mixture at C-2 of the corresponding alcohol (**30**) (436 mg) which, without purification, was used in the next reaction. IR: 3600, 3325br, 1667, 1619, 1591 cm^{-1}; ^1H NMR (60 MHz): δ=1.33 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.38 and 1.43 (3H, each s, C_3-CH_3), 2.60 (3H, s, C_4-CH_3), 2.63 (3H, s, C_9-COCH_3), 3.02 (1H, m, $-C\underline{H}(CH_3)_2$), 3.17 and 3.24 (3H, each s, $-OCH_3$), *ca.* 3.05—3.35 (2H, m, $-C\underline{H}_2OMe$), 5.49 (1H, bs, C_2–H), 7.16 (1H, dd, J=2 and 9 Hz, C_6–H), 7.78 (1H, d, J=9 Hz, C_5–H), 8.07 (1H, d, J=2 Hz, C_8–H).

A solution of the above crude **30** (436 mg) in acetone (20 ml) was oxidized with Jones' reagent (2 M: 0.8 ml) at 0—5 °C

for 45 min. After the usual work-up, the crude product was chromatographed on silica gel (45 g), using ether–benzene (3 : 97) as the eluent, to give **31** (300 mg: 69.4% from **29**). $[\alpha]_D$ +11° (*c* 4.76); IR: 1805, 1685, 1627, 1597 cm^{-1}; ^1H NMR (60 MHz): δ=1.33 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.63 (3H, s, C_3-CH_3), 2.65 (3H, s, C_4-CH_3), 2.71 (3H, s, C_9-COCH_3), 3.03 (1H, m, $-C\underline{H}(CH_3)_2$), 3.13 (3H, s, $-OCH_3$), 3.15 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 7.32 (1H, dd, J=2 and 9 Hz, C_6–H), 7.84 (1H, d, J=9 Hz, C_5–H), 8.07 (1H, d, J=2 Hz, C_8–H). Found: C, 74.77; H, 7.90%. Calcd for $C_{23}H_{28}O_4$: C, 74.97; H, 7.66%.

Oxidation of ***31*** *with* m-*Chloroperbenzoic Acid.* A mixture of **31** (3490 mg), *m*-chloroperbenzoic acid (85%: 8170 mg), and *p*-toluenesulfonic acid monohydrate (175 mg) in dichloromethane (240 ml) was refluxed for 30 h and then diluted with ether. The ether solution was washed successively with aqueous potassium iodide, aqueous sodium thiosulfate, aqueous sodium hydrogencarbonate, and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (130 g), using ether–benzene (2 : 98) as the eluent, to give (*R*)-9-acetoxy-2,3-dihydro-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]-furan-2-one (**32**) (395 mg: 10.8%). $[\alpha]_D$ +16° (*c* 1.40); IR: 1807, 1773, 1655, 1623 cm^{-1}; ^1H NMR (60 MHz): δ=1.34 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.64 (3H, s, C_3-CH_3), 2.45 (3H, s, $-OCOCH_3$), 2.62 (3H, s, C_4-CH_3), 2.98 (1H, m, $-C\underline{H}(CH_3)_2$), 3.15 (3H, s, $-OCH_3$), 3.16 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 7.37 (1H, dd, J=2 and 9 Hz, C_6–H), 7.62 (1H, bs, C_8–H), 7.94 (1H, d, J=9 Hz, C_5–H). Found: C, 72.12; H, 7.37%. Calcd for $C_{23}H_{28}O_5$: C, 71.85; H, 7.34%. Subsequent elution gave a mixture of **32** and the starting **31** (1320 mg), whose purification is described later. Further elution gave (*R*)-9-acetoxy-2,3,5,8-tetrahydro-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho [2,3-*b*] furan-2,5,8-trione (**33**) (162 mg: 4.1%). $[\alpha]_D$ +25° (*c* 1.01); IR: 1821, 1779, 1659, 1633, 1607, 1562 cm^{-1}; ^1H NMR (60 MHz): δ=1.20 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.63 (3H, s, C_3-CH_3), 2.42 (3H, s, $-OCOCH_3$), 2.68 (3H, s, C_4-CH_3), 3.04 (1H, m, $-C\underline{H}(CH_3)_2$), 3.16 (3H, s, $-OCH_3$), 3.20 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 6.55 (1H, d, J=1.5 Hz, C_6–H). Found: C, 66.83; H, 6.38%. Calcd for $C_{23}H_{26}O_7$: C, 66.65; H, 6.32%.

The above mixture (1320 mg) of **31** and **32** was treated with dilute hydrochloric acid (6 M: 8.0 ml) in refluxing methanol (50 ml) for 1 h. The mixture was concentrated *in vacuo*, diluted with 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 (120 g), using ether–benzene (5 : 95) as the eluent, to give the starting **31** (541 mg: 15.5%) and (*R*)-2,3-dihydro-9-hydroxy-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-*b*]furan-2-one (**34**) (706 mg: 21.8%); IR: 3570, 3340br, 1793, 1653, 1620, 1603 cm^{-1}; ^1H NMR (60 MHz): δ=1.33 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.59 (3H, s, C_3-CH_3), 2.48 (3H, s, C_4-CH_3), 3.18 (3H, s, $-OCH_3$), 7.21 (1H, bd, J=9 Hz, C_6–H), 7.30 (1H, br, –OH), 7.63 (1H, d, J=9 Hz, C_5–H), 7.98 (1H, bs, C_8–H).

A solution of **34** (2.01 g) and acetic anhydride (2.0 ml) in pyridine (2.0 ml) was allowed to stand at room temperature for 1 h. After the usual work-up, the crude product was chromatographed on silica gel (100 g) to give **32** (1.96 g: 86.9%).

*(R)-5,8,9-Triacetoxy-2,3-dihydro-7-isopropyl-3-(3-methoxypropyl)-3,4-dimethylnaphtho[2,3-b]furan-2-one (****35****).* Zinc powder (65 mg) was added to a stirred solution of **33** (85 mg) and acetic anhydride (0.4 ml) in pyridine (0.4 ml) at 0—5 °C. The mixture was stirred at room temperature for 1 h and then treated as described for the preparation of **7**. The crude product was chromatographed on silica gel (30 g), using ether–benzene (1 : 9) as the eluent, to give **35** (46 mg: 45%). $[\alpha]_D$ +18° (*c* 2.33); IR: 1818, 1767, 1654,1628 cm^{-1}; ^1H NMR: δ=1.22 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.59 (3H, s, C_3-CH_3), 2.29, 2.30, and 2.32 (each 3H and s, $C_5-OCOCH_3$, $C_8-OCOCH_3$, and $C_9-OCOCH_3$), 2.67 (3H, s, C_4-CH_3), 3.07 (2H, t, J=6 Hz, $-C\underline{H}_2OMe$), 3.07 (1H, m, $-C\underline{H}(CH_3)_2$), 3.09 (3H, s, $-OCH_3$), 6.96 (1H, s, C_6–H). Found: C, 65.02; H, 6.48%. Calcd for $C_{27}H_{32}O_9$: C, 64.79; H, 6.44%.

*(R)-6-Acetoxy-2,3-dihydro-7-isopropyl-3,4-dimethyl-3-[3-(o-nitrophenylseleno)propyl]naphtho[2,3-b]furan-2-one (****37****).* Tributylphosphine (0.75 ml) was added to a stirred mixture of **8** (242 mg) and *o*-nitrophenyl selenocyanate (665 mg) in pyridine (6.0 ml) at room temperature under a stream of nitrogen. The mixture was stirred at room temperature for 1 h, diluted with ether, and then filtered to remove yellow precipitates. The filtrate was evaporated *in vacuo* to give a crude selenide (**36**), which was immediately acetylated with acetic anhydride (1.0 ml) in pyridine (1.0 ml) at room temperature for 1 h. After the usual work-up, the product was purified by column chromatography on silica gel (150 g), using benzene as the eluent, to give **37** (229 mg: 56.0%). $[\alpha]_D$ +47° (*c* 2.83); IR: 1793, 1752, 1638, 1600, 1588, 1567, 1507, 1330 cm^{-1}; ^1H NMR ($CDCl_3$): δ=1.32 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.64 (3H, s, C_3-CH_3), 2.40 (3H, s, $-OCOCH_3$), 2.55 (3H, s, C_4-CH_3), *ca.* 2.5—3.0 (2H, m, $-C\underline{H}_2SeC_6H_4-$), 3.11 (1H, m, $-C\underline{H}(CH_3)_2$) *ca.* 7.0—7.2 (3H, m) and *ca.* 8.0—8.25 (1H, m) ($-SeC_6\underline{H}_4-$), 7.29 (1H, s, C_9–H), 7.56 (1H, s, C_5–H), 7.66 (1H, s, C_8–H).

*(R)-6-Acetoxy-3-allyl-2,3-dihydro-7-isopropyl-3,4-dimethylnaphtho[2,3-b]furan-2-one (****38****).* A mixture of **37** (229 mg) and 50% hydrogen peroxide (0.26 ml) in tetrahydrofuran (9.2 ml) was stirred at room temperature for 19 h. The mixture was diluted with brine and extracted with ether. The ether extract was washed successively with aqueous potassium iodide, aqueous sodium thiosulfate, aqueous sodium hydrogencarbonate, and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (15 g), using benzene as the eluent, to give **38** (129 mg: 88.6%). $[\alpha]_D$ +105° (*c* 2.82); IR: 1794, 1753, 1640, 1622 cm^{-1}; ^1H NMR: δ=1.30 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.61 (3H, s, C_3-CH_3), 2.32 (3H, s, $-OCOCH_3$), 2.62 (3H, s, C_4-CH_3), 2.76 (2H, d, J=6.5 Hz, $C_3-C\underline{H}_2CH=CH_2$), *ca.* 4.7—5.6 (3H, m, $C_3-CH_2C\underline{H}=C\underline{H}_2$), 7.20 (1H, s, C_9–H), 7.50 (1H, s, C_5–H), 7.58 (1H, s, C_8–H). Found: C, 75.27; H, 7.07%. Calcd for $C_{22}H_{24}O_4$: C, 74.97; H, 6.86%.

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