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Furan Derivatives. IV. On the Effects of Substituents in the Syntheses of 4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furans

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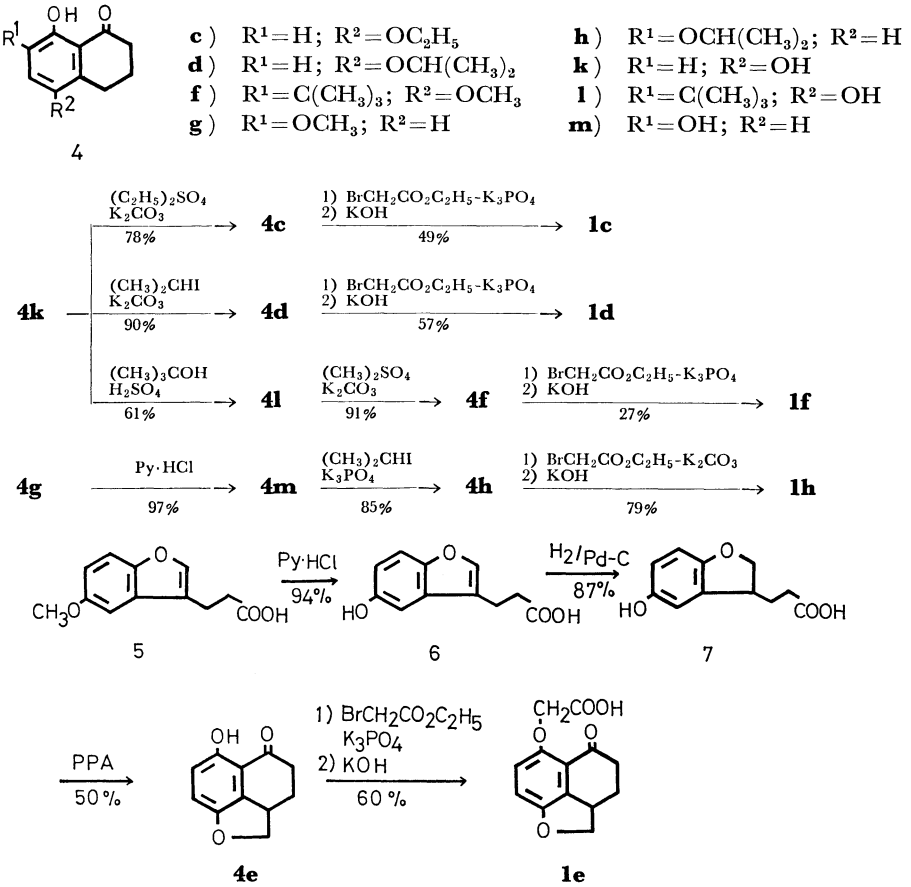
The reaction of (8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetic acids with acetic anhydride and sodium acetate give a mixture of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans and lactones. The relative yields of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans and lactones varied according to kinds of substituents on the benzene ring of (8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetic acids. Substituents which make the methylene group approach closer to the carbony carbon atom of (8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetic acids by a steric effect seem to favor the production of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans. On the other hand, substituents which make the methylene group separate from the carbonyl carbon atom seem to favor the production of lactones. An electron-withdrawing chlorine atom on the benzene ring of (8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetic acids also favors the production of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans.

4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furans (**2**) are important intermediates for the syntheses of phenanthro[4,5-*bcd*]furan derivatives.[1] 4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furans (**2**)[2] have been synthesized by heating (8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetic acids (**1**) with acetic anhydride and sodium acetate. However, the yields of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]-furans (**2**) were not good because lactones (**3**) were obtained as by-products. Formation of a considerable amount of lactones (**3**) may be due to the long distance between the methylene group adjacent to the carboxyl group and the carbonyl carbon atom of **1**, since the peri-positions in a naphthalene skeleton are too far apart for the formation of the five-membered furan ring.[3] The relative yields of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans (**2**) and lactones (**3**) varied according to kinds of substituents (R^1 and R^2). In the present investigation we examined the factors which influenced relative yields of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans (**2**) and lactones (**3**); the steric influence of R^1 and R^2 was examined in detail.

Results and Discussion

Some (8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetic acid (**1a**—**j**) were prepared to investigate the in-

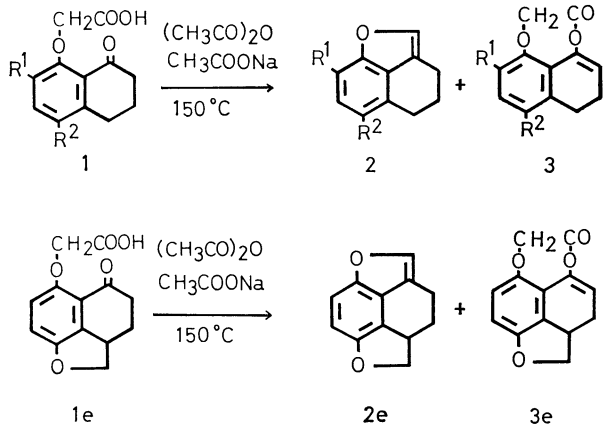


Scheme 1. The synthetic pathways of (8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetic acids (**1c**, **1d**, **1e**, **1f**, and **1h**).

fluence of substituents (R^1 and R^2) in the syntheses of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans (**2a—j**) and lactones (**3a—j**). The syntheses of **1a**, **1b**, **1g**, **1i**, and **1j** were carried out according to the methods reported.[2] The synthetic methods of **1c**, **1d**, **1e**, **1f**, and **1h** are summarized in Scheme 1.

When (8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetic acids (**1a—j**) were heated at 150 °C with acetic anhydride and sodium acetate for 1 h, 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans (**2a—d** and **2f—j**) and lactones (**3a—j**) were obtained. The relative yields and isolated yields of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans (**2a—j**) and lactones (**3a—j**) are summarized in Table 1.

Table 1. The reaction of (8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetic acids (**1a—j**) with acetic anhydride and sodium acetate



a) R^1=H; R^2=H, **b**) R^1=H; R^2=OCH_3, **c**) R^1=H; R^2=OC_2H_5, **d**) R^1=H; R^2=$OCH(CH_3)_2$, **f**) R^1=$C(CH_3)_3$; R^2=OCH_3, **g**) R^1=OCH_3; R^2=H, **h**) R^1=$OCH(CH_3)_2$; R^2=H, **i**) R^1=OCH_3; R^2=CH_3, **j**) R^1=OCH_3; R^2=Cl.

Starting materials	Product[a]	Relative yields/%	Isolated yields/%
1a	**2a**	48	37
	3a	52	40[b]
1b	**2b**	51	41
	3b	49	40
1c	**2c**	47	37
	3c	53	41
1d	**2d**	49	38
	3d	51	40
1e	**2e**	0	0
	3e	100	48[c]
1f	**2f**	92	77
	3f	8	7
1g	**2g**	65	50
	3g	35	27
1h	**2h**	60	50
	3h	40	33
1i	**2i**	67	60
	3i	33	30[a]
1j	**2j**	87	72
	3j	13	11

a) 4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furans (**2**) and lactones (**3**) are stable under the reaction conditions. b) The lactone was hydrolyzed to the starting material during isolation. c) The yield is low because of the easy hydrolysis of the lactone during isolation.

The results of Table 1 suggest the following conclusions. The reaction of **1a** (R^1=H; R^2=H) with acetic anhydride and sodium acetate gave an almost equal amount of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan (**2a**) and a lactone (**3a**) in relative yields of 48 and 52%. Similarly, in the case of **1b—d** (R^1=H; R^2=OCH_3, OC_2H_5, or $OCH(CH_3)_2$), the relative yields of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans (**2b—d**) and lactones (**3b—d**) were almost the same in spite of the various kinds of substituents R^2. This suggests that the steric or electronic effect of substituents R^2 have no influence on the relative yields of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans (**2a—d**) and lactones (**3a—d**). On the other hand, compound **1e**, in which the electronic effect of a substituent will be similar to that of **1b—d**, gave only a lactone (**3e**) and no 2,2a,3,4-tetrahydronaphtho[1,8-*bc*:4,5-*b'c'*]difuran (**2e**) was obtained. In the case of **1e**, the distance between the methylene group and the carbonyl carbon atom will be longer than that in **1a—d** because the five-membered furan ring of **1e** separates opposite peri-positions in the partially saturated naphthalene skeleton.[3] Therefore, the production of **2e** will be difficult because of the strain in the five-membered furan ring. However, the production of **3e** is not so affected by strain owing to formation of the seven-membered lactone ring. The reaction of **1f** (R^1=$C(CH_3)_3$; R^2=OCH_3) with acetic anhydride and sodium acetate gave 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan (**2f**) and a lactone (**3f**) in the relative yields of 92 and 8% respectively. The large steric effect of the *t*-butyl group in **1f** will make the methylene group approach[4] closer to the carbonyl carbon atom and will favor formation of the five-membered 4,5-dihydro-3*H*-naphtho[1,8-*bc*]-furan (**2f**). The steric repulsion between the *t*-butyl group and the methylene group is observed in the difficult etherification of **4f** with ethyl bromoacetate. The electronic effect of the *t*-butyl group will be negligible.

The reaction of **1g—h** (R^1=OCH_3 or $OCH(CH_3)_2$; R^2=H) with acetic anhydride and sodium acetate gave mainly 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans (**2g—h**) in the relative yields of 65 and 60% respectively; the yields of lactones (**3g—h**) were 35% and 40% respectively. The steric effect of the methoxyl or isopropoxyl group seems to favor the production of 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans (**2g—h**), though the substituents are not so bulky as is the *t*-butyl group.

The reaction of **1i** (R^1=OCH_3; R^2=CH_3) with acetic anhydride and sodium acetate gave 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan (**2i**) and a lactone (**3i**) in the relative yields of 67 and 33% respectively. These yields are similar to those of **2g—h** and **3g—h** and so the effect of the methyl group of **2i** is small. On the other hand, **1j** (R^1=OCH_3; R^2=Cl) with acetic anhydride and sodium acetate gave mostly 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan (**2j**; 87%) and the yield of a lactone (**3j**) was very low (13%). The electronegative chlorine atom will pull electrons from the benzene ring of **1j** and make the carbonyl carbon

atom more reactive. Therefore, formation of the 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan (**2j**) will be more favorable than that of the lactone (**3j**).

Experimental

All the melting points are uncorrected. The column chromatography was performed on silica gel (Wakogel C-200). Unless otherwise stated, anhydrous sodium sulfate was employed as the drying agent. The infrared absorption spectra were determined with a Hitachi Model EPI-G grating infrared spectrophotometer. The ultraviolet absorption spectra were determined with a Shimadzu UV-200 spectrophotometer. The nuclear magnetic resonance spectra (^{1}H NMR) were determined at 90 MHz with a JEOL Model JNM-FX 90Q FT NMR spectrometer, using tetrametylsilane as the internal standard.

*A General Procedure for the Reactions of (8-Oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetic Acids (**1**) with Acetic Anhydride and Sodium Acetate.* A mixture of **1** (1.0 g), acetic anhydride (15 ml), and sodium acetate (4.6 g) was refluxed at 150 °C for 1 h. The mixture was poured into ice–water, stirred for 5 min to decompose excess acetic anhydride, and extracted with ether. The ethereal solution was washed with a 10% potassium carbonate solution and then with water, dried, and evaporated. The resulting oil was chromatographed and eluted with benzene. The first fraction gave 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans (**2**). The second fraction afforded lactones (**3**).

*6-Ethoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan (**2c**).* Colorless oil (37% yield); bp 171 °C at 20 Torr (1 Torr≈133.322 Pa). ^{1}H NMR ($CDCl_3$): δ 1.38 (3H, t, J=7 Hz, CH_3), 1.83—2.10 (2H, m, $-CH_2-$), 2.67—2.89 (4H, m, $-CH_2-+-CH_2-$), 4.03 (2H, q, J=7 Hz, $-CH_2-$), 6.78 (1H, d, J=9 Hz, Ar–H), 7.12 (1H, dd, J=1 and 9 Hz, Ar–H), 7.24 (1H, d, J=1 Hz, furan H). UV(EtOH): λ_{max} (ε) 214 (23100), 253 (9200), 291 (2600), 302 nm (2000). Found: C, 77.02; H, 6.83%. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%.

*Lactone (**3c**).* Colorless needles from benzene–hexane (41% yield); mp 87—88 °C. IR (KBr): ν_{max} 1650 (C=C), 1765 cm^{-1} (–COO–). ^{1}H NMR (CD_3COCD_3): δ 1.36 (3H, t, J=7 Hz, CH_3), 2.15—2.41 (2H, m, $-CH_2-$), 2.76 (2H, t, J=8 Hz, $-CH_2-$), 4.03 (2H, q, J=7 Hz, $-CH_2-$), 4.71 (2H, s, $-OCH_2-$), 5.87 (1H, t, J=5 Hz, –OC=CH–), 6.78 (1H, d, J=9 Hz, Ar–H), 6.92 (1H, d, J=9 Hz, Ar–H). Found: C, 68.01; H, 5.49%. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73%.

*6-Isopropoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan (**2d**).* Colorless plates from methanol (38% yield); mp 68—69 °C. ^{1}H NMR ($CDCl_3$): δ 1.31 (6H, d, J=6 Hz, $C(CH_3)_2$), 1.96 (2H, dt, J=7 and 7 Hz, $-CH_2-$), 2.75 (2H, t, J=7 Hz, $-CH_2-$), 2.82 (2H, t, J=7 Hz, $-CH_2-$), 4.37 (1H, m, =CH–), 6.82 (1H, d, J=8 Hz, Ar–H), 7.12 (1H, d, J=8 Hz, Ar–H), 7.24 (1H, s, furan H). UV (EtOH): λ_{max} (ε) 214 (24200), 253 (9400), 292 (2100), 305 nm (1100). Found: C, 77.53; H, 7.29%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

*Lactone (**3d**).* Colorless needles from benzene–hexane (40% yield); mp 90—91 °C. IR (KBr): ν_{max} 1665 (C=C), 1780 cm^{-1} (–COO–). ^{1}H NMR (CD_3COCD_3): δ 1.29 (6H, d, J=6 Hz, $C(CH_3)_2$), 2.17—2.40 (2H, m, $-CH_2-$), 2.57—2.97 (2H, m, $-CH_2-$), 4.49 (1H, m, =CH–), 4.72 (2H, s, $-OCH_2-$), 5.87 (1H, t, J=5 Hz, –OC=CH–), 6.78 (1H, d, J=9 Hz, Ar–H), 6.95 (1H, d, J=9 Hz, Ar–H). Found: C, 68.98; H, 6.09%. Calcd for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20%.

*Lactone (**3e**).* Colorless needles from benzene–hexane (48% yield); mp 104—105 °C. IR (KBr): ν_{max} 1660 (C=C), 1760 cm^{-1} (–COO–). ^{1}H NMR (CD_3COCD_3): δ 2.12—2.86 (4H, m, $-CH_2-+-CH_2-$), 3.46—3.93 (1H, m, =CH–), 4.20 (1H, dd, J=9 and 12 Hz, –OCH=), 4.54—4.95 (3H, m, $-CH_2-+-$OCH=), 5.70 (1H, dd, J=3 and 7 Hz, –OCH=), 6.60 (1H, d, J=8 Hz, Ar–H), 6.72 (1H, dd, J=1 and 8 Hz, Ar–H). Found: C, 67.56; H, 4.41%. Calcd for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38%.

*6-Methoxy-8-t-butyl-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan (**2f**).* Colorless needles (72% yield); mp 45—46 °C. ^{1}H NMR ($CDCl_3$): δ 1.48 (9H, s, $C(CH_3)_3$), 1.95 (2H, dt, J=6 and 6 Hz, $-CH_2-$), 2.73 (2H, t, J=6 Hz, $-CH_2-$), 2.80 (2H, t, J=6 Hz, $-CH_2-$), 3.85 (3H, s, CH_3), 6.75 (1H, s, Ar–H), 7.26 (1H, s, furan H). UV (EtOH): λ_{max} (ε) 216 (25700), 252 (9800), 292 (3100), 302 nm (2600). Found: C, 78.61; H, 8.21%. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25%.

*Lactone (**3f**).* Colorless plates (7% yield); mp 105—106 °C. IR (KBr): ν_{max} 1650 (C=C), 1770 cm^{-1} (–COO–). ^{1}H NMR (CD_3COCD_3): δ 1.37 (9H, s, $C(CH_3)_3$), 2.22—2.38 (2H, m, $-CH_2-$), 2.63—2.79 (2H, m, $-CH_2-$), 3.83 (3H, s, OCH_3), 4.77 (2H, s, $-OCH_2-$), 5.87 (1H, t, J=5 Hz, –OC=CH–), 6.93 (1H, s, Ar–H). Found: C, 70.65; H, 6.83%. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99%.

*8-Isopropoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan (**2h**).* Colorless oil (50% yield); bp 178 °C at 20 Torr. ^{1}H NMR ($CDCl_3$): δ 1.37 (6H, d, J=6 Hz, $C(CH_3)_2$), 1.97 (2H, dt, J=6 and 6 Hz, $-CH_2-$), 2.74 (2H, t, J=6 Hz, $-CH_2-$), 2.81 (2H, t, J=6 Hz, $-CH_2-$), 4.83 (1H, m, =CH–), 6.70 (1H, d, J=8 Hz, Ar–H), 6.84 (1H, d, J=8 Hz, Ar–H), 7.25 (1H, s, furan H). UV (EtOH): λ_{max} (ε) 217 (29200), 249 (10300), 255 (9600), 281 (1600), 291 nm (1100). Found: C, 77.84; H, 7.46%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

*Lactone (**3h**).* Colorless oil (33% yield); bp>200 °C at 2 Torr. IR (neat): ν_{max} 1650 (C=C), 1780 cm^{-1} (–COO–). ^{1}H NMR (CD_3COCD_3): δ 1.27 (6H, d, J=6 Hz, $C(CH_3)_3$), 2.17—2.41 (2H, m, $-CH_2-$), 2.62—2.80 (2H, m, $-CH_2-$), 4.46 (1H, m, =CH–), 4.78 (2H, s, $-OCH_2-$), 5.87 (1H, t, J=5 Hz, –OC=CH–), 6.86 (2H, s, Ar–H). Found: C. 69.04; H, 6.12%. Calcd for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20%.

*8-Methoxy-6-methyl-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan (**2i**).* Colorless prisms from hexane (60% yield); mp 42—43 °C. ^{1}H NMR (CCl_4): δ 1.82—2.07 (2H, m, $-CH_2-$), 2.22 (3H, s, Ar–CH_3), 2.59—2.76 (4H, m, $-CH_2-+-CH_2-$), 3.95 (3H, s, Ar–OCH_3), 6.41 (1H, s, Ar–H), 7.17 (1H, s, furan H). UV (EtOH): λ_{max} (ε) 217 (3200), 248 (9900), 255 (9400), 284 (2000), 295 nm (1800). Found: C, 77.10; H, 7.06%. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%. The physical properties of **2a**, **2b**, **2g**, **2j**, **3b**, **3g**, and **3j** are described in Ref. 2.

*5-Ethoxy-8-hydroxy-1,2,3,4-tetrahydro-1-naphthalenone (**4c**).* A mixture of **4k** (10 g), diethyl sulfate (11 g), potassium carbonate (17 g), and acetone (100 ml) was refluxed for 6 h. The acetone was distilled off and water was added to the mixture. The mixture was refluxed for 0.5 h to decompose the excess diethyl sulfate and extracted with ether. The ethereal solution was washed with water, dried, and evaporated. The residue was chromatographed and eluted with benzene to give 11.2 g (96%) of **4c**. Recrystallization from methanol gave yellow plates; mp 61.5—62.5 °C. IR (KBr): ν_{max} 1645 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 1.38 (3H, t, J=7 Hz, CH_3), 2.05 (2H, dt, J=6 and 6 Hz, $-CH_2-$), 2.65 (2H, t, J=6 Hz, $-CH_2-$), 2.89 (2H, t, J=6 Hz, $-CH_2-$), 3.98 (2H, q, J=7 Hz, $-CH_2-$), 6.72 (1H, d, J=9 Hz, Ar–H), 7.05 (1H, d, J=9 Hz, Ar–H), 11.90 (1H, broad s, Ar–OH). Found: C, 69.75; H, 7.12%. Calcd for $C_{12}H_{14}O_3$:

C, 69.88; H, 6.84%.

*8-Hydroxy-5-isopropoxy-1,2,3,4-tetrahydro-1-naphthalenone (**4d**).* A mixture of **4k** (5.0 g), isopropyl iodide (10 g), potassium carbonate (10 g), and acetone (70 ml) was refluxed.[5] After 1 h, isopropyl iodide (5 g) and potassium carbonate (5 g) were added and the mixture was refluxed for additional 9 h. After removal of the acetone, the residue was extracted with ether. The ethereal solution was washed with water, dried, and evaporated. The resulting oil was chromatographed and eluted with benzene to give 5.6 g (90%) of **4d**. Recrystallization from methanol gave yellow plates; mp 55—56 °C. IR (KBr): ν_{max} 1645 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 1.30 (6H, d, J=7 Hz, $C(CH_3)_2$), 1.97 (2H, dt, J=6 and 6 Hz, $-CH_2-$), 2.64 (2H, t, J=6 Hz, $-CH_2-$), 2.88 (2H, t, J=6 Hz, $-CH_2-$), 4.20—4.47 (1H, m, =CH–), 6.72 (1H, d, J=9 Hz, Ar–H), 7.07 (1H, d, J=9 Hz, Ar–H), 12.00 (1H, s, Ar–OH). Found: C, 70.95; H, 7.30%. Calcd for $C_{13}H_{16}O_3$: C. 70.89; H, 7.32%.

*5,8-Dihydroxy-7-t-butyl-1,2,3,4-tetrahydro-1-naphthalenone (**4l**).* To a *t*-butyl alcohol solution (20 ml) of **4k** (2.0 g) concentrated sulfuric acid (20 g) was gradually added with stirring under cooling with ice–water.[6] The mixture was stirred for 0.5 h, decomposed with ice–water, and extracted with ether. The ethereal solution was washed with water, dried, and evaporated. A high boiling oil was removed by reduced distillation (*ca.* 140 °C at 30 Torr). The residue was chromatographed and eluted with benzene(9)–ether(1) to give 1.6 g (61%) of **4l**. Recrystallization from benzene–hexane gave yellow plates; mp 154—155 °C. IR (KBr): ν_{max} 1615 (C=O), 3360 cm^{-1} (Ar–OH). ^1H NMR ($CDCl_3$): δ 1.38 (9H, s, $C(CH_3)_3$), 1.92—2.20 (2H, m, $-CH_2-$), 2.67 (2H, t, J=7 Hz, $-CH_2-$), 2.83 (2H, t, J=6 Hz, $-CH_2-$), 4.69 (1H, broad s, Ar–OH), 6.02 (1H, s, Ar–H), 12.83 (1H, s, Ar–OH). Found: C, 71.75; H, 7.69%. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74%.

*8-Hydroxy-5-methoxy-7-t-butyl-1,2,3,4-tetrahydro-1-naphthalenone (**4f**).* The compound **4f** was prepared from **4l** by a method similar to the synthesis of **4c** from **4k**. Yellow needles from methanol (91% yield); mp 57—58 °C. IR (KBr): ν_{max} 1635 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 1.42 (9H, s, $C(CH_3)_3$), 2.03 (2H, dt, J=6 and 6 Hz, $-CH_2-$), 2.65 (2H, t, J=6 Hz, $-CH_2-$), 2.86 (2H, t, J=6 Hz, $-CH_2-$), 3.79 (3H, s, OCH_3), 7.13 (1H, s, Ar–H), 12.81 (1H, s, Ar–OH). Found: C, 72.70; H, 8.35%. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12%.

*(4-Ethoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetic Acid (**1c**).* A mixture of **4c** (1.0 g), ethyl bromoacetate (4.0 g), potassium phosphate (4.0 g), and dioxane (20 ml) was refluxed for 5 h.[2] After removal of potassium phosphate by filtration the dioxane was evaporated under reduced pressure. The residue was dissolved in ethanol (10 ml) and hydrolyzed with a 20% potassium hydroxide solution (50 ml). The alkaline solution was acidified with 6 M (1 M=1 mol dm^{-3}) hydrochloric acid and the resulting precipitates were extracted with ether. The ethereal solution was washed with water, dried, and evaporated. Trituration of the residue with benzene gave 0.63 g (49%) of **1c**. Recrystallization from methanol gave colorless plates; mp 140—141 °C. IR (KBr): ν_{max} 1655 (C=O), 1765, 1780 cm^{-1} (COOH). ^1H NMR (CD_3COCD_3): δ 1.40 (3H, t, J=7 Hz, CH_3), 1.92—2.20 (2H, m, $-CH_2-$), 2.65 (2H, t, J=6 Hz, $-CH_2-$), 2.92 (2H, t, J=6 Hz, $-CH_2-$), 4.08 (2H, q, J=7 Hz, $-CH_2-$), 4.70 (2H, s, $-CH_2-$), 7.01 (1H, d, J=9 Hz, Ar–H), 7.21 (1H, d, J=9 Hz, Ar–H). Found: C, 63.41; H, 6.19%. Calcd for $C_{14}H_{16}O_5$: C, 63.62; H, 6.10%.

*(4-Isopropoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetic Acid (**1d**).* The compound **1d** was prepared from **4d** by a method similar to the synthesis of **1c** from **4c**. Colorless plates from methanol (57% yield); mp 130—131 °C. IR (KBr): ν_{max} 1660 (C=O), 1765, 1785 cm^{-1} (COOH). ^1H NMR (CD_3COCD_3): δ 1.32 (6H, d, J=6 Hz, $C(CH_3)_2$), 1.92—2.19 (2H, m, $-CH_2-$), 2.65 (2H, t, J=5 Hz, $-CH_2-$), 2.90 (2H, t, J=6 Hz, $-CH_2-$), 4.58 (1H, m, =CH–), 4.71 (2H, s, $-CH_2-$), 7.00 (1H, d, J=9 Hz, Ar–H), 7.25 (1H, d, J=9 Hz, Ar–H). Found: C, 64.74; H, 6.43%. Calcd for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52%.

*(4-Methoxy-8-oxo-2-t-butyl-5,6,7,8-tetrahydro-1-naphthyloxy)acetic Acid (**1f**).* The compound **1f** was prepared from **4f** by a method similar to the synthesis of **1c** from **4c**. Colorless plates from ether–hexane (27% yield); mp 139—140 °C. IR (KBr): ν_{max} 1665 (C=O), 1770, 1785 cm^{-1} (COOH). ^1H NMR (CD_3COCD_3): δ 1.43 (9H, s, $C(CH_3)_3$), 1.97—2.17 (2H, m, $-CH_2-$), 2.59 (2H, t, J=7 Hz, $-CH_2-$), 2.84 (2H, t, J=6 Hz, $-CH_2-$), 3.88 (3H, s, OCH_3), 4.41 (2H, s, $-OCH_2-$), 7.20 (1H, s, Ar–H). Found: C, 66.41; H, 7.00%. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24%.

*7,8-Dihydroxy-1,2,3,4-tetrahydro-1-naphthalenone (**4m**).* A mixture of **4g** (1.0 g) and pyridinium chloride (10 g) was heated at 200 °C for 1 h.[7] The mixture was poured into ice–water and extracted with ether. The ethereal solution was washed with water, dried, and evaporated to give 0.90 g (97%) of **4m**. Recrystallization from benzene–hexane gave yellow plates; mp 92—93 °C. IR (KBr): ν_{max} 1640 (C=O), 3530 cm^{-1} (Ar–OH). ^1H NMR (CD_3COCD_3): 2.04 (2H, dt, J=6 and 6 Hz, $-CH_2-$), 2.65 (2H, t, J=6 Hz, $-CH_2-$), 2.85 (2H, t, J=6 Hz, $-CH_2-$), 6.62 (1H, d, J=8 Hz, Ar–H), 7.00 (1H, d, J=8 Hz, Ar–H), 7.49 (1H, s, Ar–OH), 12.51 (1H, s, Ar–OH). Found: C, 67.43; H, 5.91%. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66%.

*8-Hydroxy-7-isopropoxy-1,2,3,4-tetrahydro-1-naphthalenone (**4h**).* The compound **4h** was prepared from **4m** by a method similar to the synthesis of **4d** from **4k**. Yellow plates from hexane (85% yield); mp 74—75 °C. IR (KBr): ν_{max} 1640 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 1.34 (6H, d, J=6 Hz, $C(CH_3)_2$), 2.06 (2H, dt, J=6 and 6 Hz, $-CH_2-$), 2.65 (2H, t, J=6 Hz, $-CH_2-$), 2.86 (2H, t, J=6 Hz, $-CH_2-$), 4.50 (1H, m, =CH–), 6.59 (1H, d, J=8 Hz, Ar–H), 7.02 (1H, d, J=6 Hz, Ar–H), 12.62 (1H, s, Ar–OH). Found: C. 71.16; H, 7.39%. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%.

*(2-Isopropoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthyloxy)acetic Acid (**1h**).* The compound **1h** was prepared from **4h** by a method similar to the synthesis of **1c** from **4c**. Colorless needles from benzene–hexane (79% yield); mp 89—90 °C. IR (KBr): ν_{max} 1670, 1685 (C=O), 1760, 1775 cm^{-1} (COOH). ^1H NMR (CD_3COCD_3): δ 1.37 (6H, d, J=6 Hz, $C(CH_3)_2$), 1.91—2.18 (2H, m, $-CH_2-$), 2.67 (2H, t, J=6 Hz, $-CH_2-$), 2.94 (2H, t, J=6 Hz, $-CH_2-$), 4.46—4.80 (1H, m, =CHO–), 4.73 (2H, s, $-OCH_2-$), 7.06 (1H, d, J=8 Hz, Ar–H), 7.33 (1H, d, J=8 Hz, Ar–H). Found: C, 64.56; H, 6.68%. Calcd for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52%.

*3-(5-Hydroxybenzofuran-3-yl)propionic Acid (**6**).* A mixture of **5** (15 g) and pyridinium chloride (100 g) was heated for 1 h at 200 °C,[7] poured into ice–water, and extracted with ether. The ethereal solution was washed with 1 M hydrochloric acid and then with water, dried, and evaporated to give 17.4 g (93%) of **6**. Recrystallization from acetone–benzene gave colorless needles; mp 170—171 °C. IR (KBr): ν_{max} 1720 (COOH), 3270 cm^{-1} (Ar–OH). ^1H NMR (CD_3COCD_3): δ 2.59—3.06 (4H, m, $-CH_2-+-CH_2-$), 6.83 (1H, dd, J=2 and 9 Hz, Ar–H), 7.02 (1H, d, J=2 Hz, Ar–H), 7.27 (1H, d, J=2 Hz, Ar–H), 7.27 (1H, d, J=9 Hz, Ar–H), 7.55 (1H, s, furan H). Found: C, 64.19;

H, 4.98%. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89%.

3-(5-Hydroxy-2,3-dihydrobenzofuran-3-yl)propionic Acid (7). An ethanolic solution (50 ml) of **6** (12 g) was hydrogenated for 16 h in the presence of 7% palladium on charcoal (2.4 g) as a catalyst under 7 atm at 65 °C.[8] After removal of the catalyst by filtration the partially produced ester was hydrolyzed with a 30% potassium hydroxide solution. The alkaline solution was acidified with 6 M hydrochloric acid and extracted with ether. The ethereal solution was washed with water, dried, and evaporated to give 10.6 g (87%) of **7**. Recrystallization from acetone–benzene gave colorless needles; mp 117—118 °C. IR (KBr): ν_{max} 1750 (COOH), 3310 cm^{-1} (Ar–OH). ^1H NMR (CD_3COCD_3): δ 1.61—2.16 (2H, m, $-CH_2-$), 2.30—2.49 (2H, m, $-CH_2-$), 3.26—3.57 (1H, m, =CH–), 4.17 (1H, dd, J=6 and 9 Hz, –OCH=), 4.56 (1H, t, J=9 Hz, –OCH=), 6.56—6.76 (3H, m, Ar–H). Found: C, 63.65; H, 5.85%. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%.

6-Hydroxy-2a,3,4,5-tetrahydro-2H-naphtho[1,8-bc]furan-5-one (4e). A mixture of **7** (20 g) and polyphosphoric acid (300 g) was heated at 80 °C for 5 h under stirring.[8] The mixture was poured into ice–water and extracted with ether. The ethereal solution was washed with a 10% potassium carbonate solution and then with water, dried, and evaporated to give 9.1 g (50%) of **4e**. Recrystallization from benzene–hexane gave yellow needles; mp 123—124 °C. IR (KBr): ν_{max} 1650 (C=O), 3220 cm^{-1} (Ar–OH). ^1H NMR ($CDCl_3$): δ 1.65—2.75 (4H, m, $-CH_2-+-CH_2-$), 3.45—3.85 (1H, m, =CH–), 4.10 (1H, dd, J=9 and 11 Hz, –OCH=), 4.85 (1H, dd, J=8 and 8 Hz, –OCH=), 6.64 (1H, dd, J=1 and 9 Hz, Ar–H), 6.91 (1H, d, J=9 Hz, Ar–H), 9.86 (1H, s, Ar–H). Found: C, 69.62; H, 5.48%. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30%.

(5-Oxo-2a,3,4,5-tetrahydro-2H-naphtho[1,8-bc]furan-6-yloxy)-acetic Acid (1e). The compound **1e** was prepared from **4e** by a method similar to the synthesis of **1c** from **4c**. Colorless plates from acetone–benzene (60% yield); mp 155—156 °C. IR (KBr): ν_{max} 1670 (C=O), 1760 (COOH), 3120 cm^{-1} (COOH). ^1H NMR (CD_3COCD_3): δ 1.86—2.52 (2H, m, $-CH_2-$), 2.63—2.78 (2H, m, $-CH_2-$), 3.57—3.99 (1H, m, =CH–), 4.14 (1H, dd, J=8 and 11 Hz, –OCH=), 4.68 (2H, s, $-OCH_2-$), 4.90 (1H, dd, J=8 and 8 Hz, $-CH_2-$), 6.94 (2H, s, Ar–H). Found: C, 62.83; H, 4.69%. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87%.

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