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Furan Derivatives. III. Some Electrophilic Substitution Reactions and Hydrogenation of 4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furans

Takaaki Horaguchi* and Teishiro Abe†

Department of Chemistry, Faculty of Science, Niigata University, Ikarashi, Niigata 950-21

† *Department of General Education, Niigata University, Ikarashi, Niigata 950-21*

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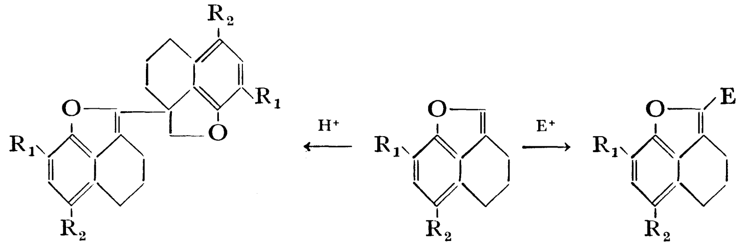
4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furans (**1a**—**d**) reacted with a variety of electrophilic reagents to give the corresponding 2-substituted 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans. Hydrogenation of **1a**—**d** gave the corresponding 2*a*,3,4,5-tetrahydro-2*H*-naphtho[1,8-*bc*]furans. 2*H*-Naphtho[1,8-*bc*]furans (**7a**—**c**) which were prepared from **1a**—**c** were gradually converted to the 8-hydroxynaphthalene-1-carbaldehydes in air. The facile cleavage of the ether bond of **7a**—**c** is thought due to ring strain in the 2*H*-naphtho[1,8-*bc*]furan ring system.

In a previous paper,[1)] the synthetic methods for 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furans (**1a**—**d**) were reported. Since the novel ring system of **1a**—**d** possesses a furan ring at the *peri*-position of a partially saturated naphthalene ring, there may be some ring strain[1b)] and so a difference in reactivity between **1a**—**d** and benzofurans is expected. In the present study, several reactions of **1a**—**d** have been examined and compared with those of the benzofurans.

Electrophilic substitution reactions and dimerization of **1a**—**d** are summarized in Table 1. Bromination of **1a**—**d** was carried out with bromine in carbon tetrachloride. Although **1b** and **1d** gave the corresponding 2-bromo compounds (**2b** and **2d**) in 89 and 74% yields, respectively, **1c** gave the corresponding 2-bromo compound (**2c**) in low yield (21%). The low yield was attributed to the formation of a resinous product. **1a** gave a complex mixture and the expected bromide was not isolated. Formylation of **1a,c,d** with *N,N*-dimethylformamide and phosphoryl chloride gave the corresponding 2-formyl compounds (**3a,c,d**). The yields of **3a** and **3c** were good (74 and 65% respectively), but **3d** gave only a 27% yield and the starting material (**1d**) was recovered; the low reactivity of **1d** is thought due to the strong inductive effect of the chlorine atom. Friedel-Crafts reaction of **1a** and **1c** was carried out with benzoyl chloride and tin(IV) chloride in carbon disulfide. The expected 2-benzoyl compounds (**4a** and **4c**) were obtained in low yields (27 and 25%, respectively) due to the formation of a resinous product. It appears that the 4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan ring is appreciably unstable under the reaction conditions. When **1a**—**d** were treated with sulfuric acid in ethanol, **1a**—**c** gave the corresponding dimers (**5a**—**c**) in good yields (56—90%), but the dimerization of **1d** did not occur. Again, the strong inductive effect of the chlorine atom of **1d** reduces the electron deisity at the 2-position in the furan ring.

These results suggest that the position of electrophilic substitution reactions of **1a**—**d** are similar to those of the benzofurans. Thus, bromination, formylation, and acylation of the 3-alkylbenzofurans occur at the 2-position of the furan ring[3)] and the dimerization of the

Table 1. Electrophilic substitution reactions and dimerization of **1a**—**d**

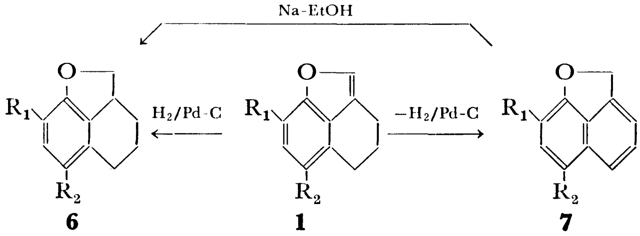


5 **1** **2**—**4**

a) $R_1=H$, $R_2=H$
b) $R_1=CH_3$, $R_2=H$
c) $R_1=H$, $R_2=OCH_3$
d) $R_1=CH_3$, $R_2=Cl$

Starting furan	Reagent	Product		Yield %
1a	Br_2	complex mixture		—
1b		**2** (E=Br)	**b**	89
1c			**c**	21
1d			**d**	74
1a	$HCON(CH_3)_2$ $POCl_3$	**3** (E=CHO)	**a**	74
1c			**c**	65
1d			**d**	27
1a	C_6H_5COCl $SnCl_4$	**4** (E=C_6H_5CO)	**a**	27
1c			**c**	25
1a	H_2SO_4	**5**	**a**	84
1b			**b**	56
1c			**c**	90
1d		no reaction		—

TABLE 2. HYDROGENATION AND DEHYDROGENATION REACTIONS OF **1a**—**d** AND **7a**—**c**



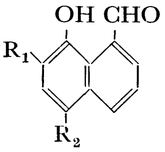
a) $R_1=H$, $R_2=H$ c) $R_1=H$, $R_2=OCH_3$
b) $R_1=OCH_3$, $R_2=H$ d) $R_1=OCH_3$, $R_2=Cl$

Starting furan	Reagent	Product	Yield %
1a	H_2/Pd-C	**6a**	98
1b		**6b**	92
1c		**6c**	97
1d		**6b**	90
1a	Pd-C	**7a**	41
1b		**7b**	58
1c		**7c**	47
1d		no reaction	—
7a	Na-EtOH	**6a**	78
7b		**6b**	73
7c		**6c**	88

3-alkylbenzofurans is achieved readily by acid catalysis.[2] However, **1a**—**d** are significantly less stable compared with the benzofurans under vigorous conditions such as acylation.

Hydrogenation and dehydrogenation reactions of **1a**—**d** are summarized in Table 2. Palladium on charcoal catalyzed hydrogenation of **1a**—**c** in ethanol at ambient temperature and pressure gave the corresponding tetrahydro compounds (**6a**—**c**) in good yields (92—98%). In the case of **1d**, the chlorine atom was subjected to hydrogenolysis along with hydrogenation of the furan ring to give **6b** (90% yield). The benzofurans subjected to hydrogenation gave the corresponding 1,2-dihydrobenzofurans under the same conditions[1a,4] and the rate of hydrogen consumption of **1a**—**d** was comparable with that of the benzofurans. If **1a**—**d** contains a larger strain compared to that of the benzofurans, the former should be more readily hydrogenated than the latter. The above results suggest that **1a**—**d** contain little strain compared with the benzofurans.

When **1a**—**c** were heated with palladium on charcoal in *p*-cymene, the corresponding 2*H*-naphtho[1,8-*bc*]-furans (**7a**—**c**) were obtained in fairly good yields (41—58%). However **1d** could not be dehydrogenated to the corresponding 2*H*-naphtho[1,8-*bc*]furan and the starting material was recovered. Thus, the reactivity of **1d** is affected by the strong inductive effect of the chlorine atom. Reduction of **7a**—**c** with sodium and ethanol gave the corresponding tetrahydro compounds (**6a**—**c**) in good yields (73—88%). Colorless compounds of **7a**—**c** are appreciably unstable and turned yellow or red upon storage; the liqiud compound **7b** gave a particullarly prominent coloration. Berry *et al.*[5] have suggested that the coloration of **7a** is due to the formation of 8-hydroxynaphthalene-1-carbaldehyde (**8a**). The cause of the coloration of both **7b** and **7c** was examined; **7b** was chromatographed over silica gel and **8b** isolated as the main colored product. Similarly, the colored material of **7c** was confirmed to be **8c**. Thus the compounds of the general type **7a**—**c** are easily subjected to cleavage of the ether bond. It has been pointed out that acenaphthene (**9**) which possesses a similar ring skeleton with **7a**—**c** contains a strain in the fused ring system.[6] Therefore, the facile cleavage of the ether bond of **7a**—**c** is thought due to ring strain in the 2*H*-naphtho[1,8-*bc*]furan ring system.



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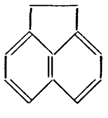
a) $R_1=H$, $R_2=H$
b) $R_1=OCH_3$, $R_2=H$
c) $R_1=H$, $R_2=OCH_3$



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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 JASCO Model DS 402 G infrared spectrophotometer. The ultraviolet absorption spectra were determined with a Shimadzu Model UV-200 spectrophotometer. The nuclear magnetic resonance spectra were determined at 100 MHz with a JEOL Model 4H-100 NMR spectrometer, using tetramethyl silane as the internal standard.

*Bromination of 4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furans (1a—d).* Bromine (0.85 g) in carbon tetrachloride (10 ml) was added dropwise to **1b** (1.0 g) in carbon tetrachloride (10 ml) with stirring at ambient temperature and the mixture further stirred for 30 min. After the removal of the solvent, the resulting oil was chromatographed and eluted with benzene to give **2b** (1.2 g, 89%). Colorless oil; bp 135 °C/1.5 Torr (partially decomposed). NMR(CCl_4): δ 1.85—2.09 (2H, m), 2.55—2.80 (4H, m), 3.96 (3H, s), 6.51 (1H, d, J=8 Hz), 6.71 (1H, d, J=8 Hz). Found: C, 53.88; H, 4.26%. Calcd for $C_{12}H_{11}O_2Br$: C, 53.96; H, 4.15%.

Similarly, **1c** and **1d** were brominated to give **2c** and **2d** (21 and 74%), respectively; **1a** was brominated to give a complex mixture and the simple bromide was not isolated.

2c: Colorless needles; mp 52—53 °C (from hexane). NMR(CCl_4): δ 1.85—2.08 (2H, m), 2.61 (2H, t, J=6 Hz), 2.73 (2H, t, J=6 Hz), 3.79 (3H, s), 6.61 (1H, d, J=8 Hz), 7.01 (1H d, J=8 Hz).
Found: C, 53.85; H, 4.20%. Calcd for $C_{12}H_{11}O_2Br$: C, 53.96; H, 4.15%.

2d: Colorless needles; mp 109—110 °C (from hexane). NMR (CCl_4): δ 1.87—2.11 (2H, m), 2.61 (2H, t, J=6 Hz), 2.75 (2H, t, J=6 Hz), 3.97 (3H, s), 6.55 (1H, s). Found: C, 47.68; H, 3.46%. Calcd for $C_{12}H_{10}O_2BrCl$: C, 47.79; H, 3.34%.

*Formylation of 4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furans (1a,c,d).* Phosphoryl chloride (2.7 g) in *N,N*-dimethylformamide (4.5 g) was added to **1a** (1.5 g) in *N,N*-dimethylformamide (6.0 g) and the mixture heated at 90 °C for 3 h. The reaction mixture was then poured into ice water and allowed to stand overnight. The resulting precipitates were collected by filtration to give **3a** (1.3 g, 74%), which was purified by recrystallization. Yellow needles; mp 88—89 °C (from methanol). IR(KBr): ν_{max} 1680 (CHO) cm^{-1}. NMR(CDCl$_3$): δ 1.97—2.22 (2H, m), 2.93 (2H, t, J=6 Hz), 3.10 (2H, t, J=6 Hz), 6.98—7.48 (3H, m), 9.87 (1H, s). UV(EtOH): λ_{max} (ε) 203 (14300), 233^{sh} (9100), 238 (10000), 304 nm (22300). Found: C, 77.13; H, 5.41%. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41%.

Similarly, **1c** and **1d** were formylated to give **3c** and **3d** (65 and 27%), respectively.

3c: Yellow needles; mp 154—155 °C (from ethanol). IR(KBr): ν_{max} 1680 (CHO) cm^{-1}. NMR(CDCl$_3$): δ 1.93—2.18 (2H, m), 2.86 (2H, t, J=6 Hz), 3.06 (2H, t, J=6 Hz), 3.86 (3H, s), 7.03 (1H, d, J=9 Hz), 7.22 (1H, d, J=9 Hz), 9.85 (1H, s). UV(EtOH): λ_{max} (ε) 206 (19500), 224^{sh} (10300) 306 nm (24000). Found: C, 72.02; H, 5.68%. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59%.

3d: Yellow needles; mp 171—172 °C (from methanol). IR(KBr): ν_{max} 1675 (CHO) cm^{-1}. NMR(CDCl$_3$): δ 1.95—2.20 (2H, m), 2.85 (2H, t, J=6 Hz), 3.07 (2H, t, J=6 Hz), 4.00 (3H, s), 6.87 (1H, s), 9.92 (1H, s). UV(EtOH): λ_{max} (ε) 206 (28900), 247 (17000), 301 nm (19700). Found: C, 62.07; H, 4.52%. Calcd for $C_{13}H_{11}O_3Cl$: C, 62.29; H, 4.42%.

*Benzoylation of 4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furans (**1a** and **1c**).* Tin(IV) chloride (2.0 g) was added to a solution of **1a** (1.0 g) and benzoyl chloride (1.1 g) in carbon disulfide (10 ml) under cooling with ice water and stirring, and the mixtures was further stirred at ambient temperature for 3 h. After the addition of diluted hydrochloric acid, the mixture was extracted with ether, ethereal layer washed successively with aqueous sodium hydrogencarbonate and water, and dried. After removal of the solvent, the resulting oil was chromatographed and eluted with benzene to give **4a** (0.44 g, 27%), which was identical with the sample previously prepared[1b] from the melting points and infrared spectra. Similarly, **1c** was benzoylated to give **4c** (25%).

4c: Colorless prisms; mp 90—91 °C (from ethanol). IR(KBr): ν_{max} 1625 (C=O) cm^{-1}. NMR(CDCl$_3$): δ 1.89—2.13 (2H, m), 2.85 (2H, t, J=6 Hz), 3.00 (2H, t, J=6 Hz), 3.85 (3H, s), 7.02 (1H, d, J=9 Hz), 7.25 (1H, d, J=9 Hz), 7.38—7.58 (4H, m), 8.01—8.11 (2H, m). UV(EtOH): λ_{max} (ε) 207 (25500), 257 (7900), 322 nm (21700). Found: C, 78.01; H, 5.64%. Calcd for $C_{18}H_{16}O_3$: C, 78.06; H, 5.52%.

*Dimerization of 4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furans (**1a—d**).* Sulfuric acid (6.0 g) was added dropwise to **1a** (1.0 g) in ethanol (4 ml) under cooling with ice water and stirring, and the mixture further stirred at ambient temperature for 3 h. The reaction mixture was then poured into ice water and the mixture extracted with ether. The ethereal layer was treated, in the usual manner, to give **5a** (0.84 g, 84%) which was purified by recrystallization. Colorless plates; mp 158—159 °C (from benzene-hexane). NMR(CCl$_4$): δ 1.60—1.90 (7H, m), 2.58—2.78 (5H, m), 4.18 (1H, d, J=8 Hz), 4.85 (1H, d, J=8 Hz), 6.52—7.13 (6H, m). UV(EtOH): λ_{max} (ε) 208 (40300), 215^{sh} (34100), 256 (16500), 286 nm (3500). Found: C, 83.40; H, 6.38%. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37%. Similarly, **1b** and **1c** were dimerized to give **5b** and **5c** (56 and 90%), respectively; **1d** was not dimerized and the starting material was recovered.

5b: Colorless plastic solid. NMR(CCl$_4$): δ 1.57—1.90 (7H, m), 2.53—2.78 (5H, m), 3.85 (3H, s), 3.94 (3H, s), 4.20 (1H, d, J=8 Hz), 4.92 (1H, d, J=8 Hz), 6.49 (1H, d, J=8 Hz), 6.53 (1H, d, J=8 Hz), 6.66 (1H, d, J=8 Hz), 6.70 (1H, d, J=8 Hz). UV(EtOH): λ_{max} (ε) 216 (46400), 249 (16300), 357 (15500), 280 (3900), 290 nm (3000). Found C, 76.80; H, 6.60%. Calcd for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43%.

5c: Colorless plates; mp 182—183 °C (from benzene-hexane). NMR(CDCl$_3$): δ 1.55—2.00 (7H, m), 2.60—2.70 (5H, m), 3.81 (6H, s), 4.21 (1H, d, J=8 Hz), 4.90 (1H, d, J=8 Hz), 6.64 (2H, s), 6.74 (1H, d, J=8 Hz), 7.10 (1H, d, J=8 Hz). UV(EtOH): λ_{max} (ε) 215^{sh} (34400), 260 (15900), 291 nm (7900). Found: C, 76.75; H, 6.54%. Calcd for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43%.

*Catalytic Hydrogenation of 4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furans (**1a—d**).* **1a** (1.0 g) in ethanol (50 ml) was hydrogenated in the presence of 10% palladium on charcoal (0.8 g) at ambient temperature and pressure for 10 h. After the removal of the catalyst by filtration, the solvent was evaporated to give **6a** (1.0 g, 98%), which distilled off at 101 °C/1 Torr and the distilate solidified in a short time. Colorless solid; mp 33—34 °C. NMR(CCl$_4$): δ 1.10—1.86 (2H, m), 1.90—2.20 (2H, m), 2.53—2.90 (2H, m), 3.00—3.37 (1H, m) 3.85 (1H, dd, J=8 and 12 Hz), 4.63 (1H, t, J=8 Hz), 6.42 (1H, d, J=8 Hz), 6.46 (1H, d, J=8 Hz), 6.88 (1H, t, J=8 Hz). Found: C, 82.21; H, 7.56%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%. Similarly, **1b** and **1c** were hydrogenated to give **6b** and **6c** (92 and 97%), respectively; **1d** was hydrogenated to give **6b** (92%) instead of **6d**.

6b: Colorless oil; bp 106 °C/1.5 Torr. NMR(CCl$_4$): δ 1.15—1.82 (2H, m), 1.92—2.20 (2H, m), 2.32—2.85 (2H, m), 3.00—3.40 (1H, m), 3.80 (3H, s), 3.86 (1H, dd, J=8 and 10 Hz), 4.67 (1H, t, J=8 Hz), 6.40 (1H, d, J=8 Hz), 6.53 (1H, d, J=8 Hz). Found: C, 75.54; H, 7.34%. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%.

6c: Colorless oil; bp 112 °C/2 Torr. NMR(CCl$_4$): δ 1.00—1.85 (2H, m), 1.93—2.22 (2H, m), 2.35—2.81 (2H, m), 2.95—3.35 (1H, m), 3.68 (3H, s), 3.80 (1H, dd, J=2 and 8 Hz), 4.59 (1H, t, J=8 Hz), 6.35 (2H, s). Found: C, 75.60; H, 7.31%. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%.

*Dehydrogenation of 4,5-Dihydro-3*H*-naphtho[1,8-*bc*]furans (**1a—d**).* A mixture of **1a** (1.8 g) and 10% palladium on charcoal (1.5 g) in *p*-cymene (20 ml) was heated at 180 °C for 4 h under a nitrogen atmosphere. The reaction mixture, after the usual treatment, was chromatographed and eluted with benzene-hexane (1:1) to give **7a** (0.73 g, 41%). Colorless plates; mp 53.5—54.5 °C (from methanol) (lit,[5] 53—54 °C). NMR(CCl$_4$): δ 5.60 (2H, s), 6.56 (1H, d, J=7 Hz), 6.97—7.50 (5H, m). UV(EtOH): λ_{max} (ε) 202 (14200), 251 (7700), 312 (8800), 340 nm (4200). Found: C, 84.44; H, 5.09%. Calcd for $C_{11}H_8O$: C, 84.59; H, 5.16%. Similarly, **1b** and **1c** were dehydrogenated to give **7b** and **7c** (58 and 47%), respectively; **1d** was not dehydrogenated and the starting material was recovered.

7b: Colorless oil; bp 96 °C/0.9 Torr. NMR(CCl$_4$): δ 4.00 (3H, s), 5.65 (2H, s), 7.01 (3H, s), 7.16 (1H, d, J=8 Hz), 7.41 (1H, d, J=8 Hz). UV(EtOH): λ_{max} (ε) 213 (21400), 238 (44000), 303 (3600), 334 nm (3200). Found: C, 77.38; H, 5.52%. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41%.

7c: Colorless needles; mp 46—47 °C (from benzene-hexane). NMR(CCl$_4$): δ 3.84 (3H, s), 5.61 (2H, s), 6.47 (1H, d, J=7 Hz), 6.50 (1H, d, J=7 Hz), 7.05 (1H, d, J=7 Hz), 7.33 (1H, t, J=7 Hz), 7.69 (1H, d, J=7 Hz). UV(EtOH): λ_{max} (ε) 207 (39300), 242 (24200), 246 (23600), 325 (7200), 339 nm (7500). Found: C, 77.13; H, 5.29%. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41%.

*Reduction of 2*H*-Naphtho[1,8-*bc*]furans (**7a—c**).* Sodium (2.0 g) was added, in limited amounts over 30 min, to **7a** (0.2 g) in ethanol (15 ml) with stirring at 80 °C and th mixture refluxed for an additional 1 h. The reaction mixture was poured into ice water, acidified with dilute hydrochloric acid and then extracted with ether. After evaporation of the ether, the resulting oil was chromatographed and eluted with benzene to give **6a** (0.16 g, 78%). Similarly, **7b** and **7c** were reduced to give **6b** and **6c** (73 and 88%), respectively.

Examination of the Coloration of 2H-*Naphtho*[*1,8*-bc]*furans (***7b** *and* **7c***).* The deeply reddish **7b** (1.0 g) was chromatographed and eluted with benzene–ether (9:1) to give **8b** (60 mg, 6%). Orange needles; mp 85—87 °C (from benzene–hexane). IR(KBr): $\nu_{\max}$ 1660 (CHO), 3290 (Ar-OH) $\mathrm{cm^{-1}}$. NMR($\mathrm{CDCl_3}$): δ 4.00 (3H, s), 7.29—7.46 (3H, m), 7.95 (2H, d, J=8 Hz), 10.08 (1H, s), 10.75 (1H, s). Found: C, 71.39; H, 5.05%. Calcd for $\mathrm{C_{12}H_{10}O_3}$: C, 71.28; H, 4.99%.

The colored material of **7c** was identical, by TLC analysis, with **8c** which was prepared from **7c** as below. A solution of **7c** (0.5 g) and lead tetraacetate (1.3 g) in acetic acid (60 ml) was stirred at ambient temperature for 4 h. The reaction mixture, after the usual treatment, was chromatographed to give **8c** (50 mg, 9%). Orange needles; mp 96—98 °C (from benzene–hexane). IR(KBr): $\nu_{\max}$ 1665 (CHO) $\mathrm{cm^{-1}}$. NMR ($\mathrm{CDCl_3}$): δ 3.95 (3H, s), 6.93 (1H, d, J=8 Hz), 7.11 (1H, d, J=8 Hz), 7.55 (1H, t, J=7 Hz), 8.05 (1H, dd, J=1 and 6 Hz), 8.67 (1H, dd, J=1 and 6 Hz), 9.87 (1H, s), 10.97 (1H, s). Found: C, 71.38; H, 5.08%. Calcd for $\mathrm{C_{12}H_{10}O_3}$: C, 71.28; H, 4.99%.

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