Notes

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Dienone–Phenol Rearrangement of (+)-2′-Demethoxydehydrogriseofulvin into a 4-Methylxanthone Derivative

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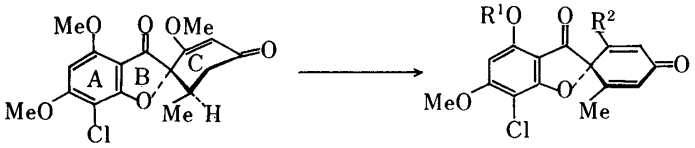
Treatment of (+)-2′-demethoxydehydrogriseofulvin (**2b**) with magnesium iodide afforded 5-chloro-2,8-dihydroxy-6-methoxy-4-methylxanthone (**3a**) *via* dienone–phenol rearrangement. The structure of **3a** was determined by means of a carbon-13 nuclear magnetic resonance (^{13}C-NMR) long-range selective proton decoupling (LSPD) experiment performed on its diacetate **3b**. The rearrangement of **2b** was also effected with *p*-toluenesulfonic acid to give 5-chloro-6,8-dimethoxy-2-hydroxy-4-methylxanthone (**6a**). On the other hand, reaction of (−)-dehydrogriseofulvin (**2d**) with *p*-toluenesulfonic acid under more vigorous conditions resulted in racemization, no rearrangement being observed.

Keywords——^{13}C-NMR long-range selective proton decoupling; 5-chloro-2,8-diacetoxy-6-methoxy-4-methylxanthone; 3-acetoxy-5-chloro-6,8-dimethoxy-1-methylxanthone; dienone–phenol rearrangement; C-migration; racemization; dehydrogriseofulvin

During the course of the studies on griseofulvin biosynthesis,[1] we attempted to prepare 2′-demethoxy-4-demethyldehydrogriseofulvin (**2a**) from **1** (Chart 1) as a synthetic intermediate in order to examine the biosynthetic pathway in a griseofulvin-producing microorganism, *Penicillium urticae*. Treatment of (+)-2′-demethoxydehydrogriseofulvin (**2b**) with magnesium iodide[2a] afforded not the desired **2a** but a rearrangement product. For



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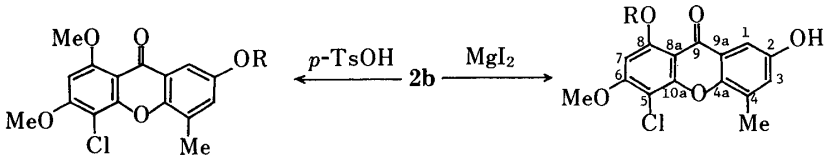
2a : $R^1=R^2=H$ **2c** : $R^1=H$, $R^2=OMe$
2b : $R^1=Me$, $R^2=H$ **2d** : $R^1=Me$, $R^2=OMe$



6a: R=H
6b: R=COMe

3a: R=H
3b: R=COMe

Chart 1

structural elucidation of the product, 3-acetoxy-5-chloro-6,8-dimethoxy-1-methylxanthone (**5c**) was synthesized from griseophenone A (3-chloro-2,2′-dihydroxy-6′-methyl-2′,4,6-trimethoxybenzophenone; **4b**) as a reference compound for the carbon-13 nuclear magnetic

resonance (^{13}C-NMR) study. The structure of the rearrangement product was determined to be 5-chloro-2,8-dihydroxy-6-methoxy-4-methylxanthone (**3a**) by means of a ^{13}C-NMR long-range selective proton decoupling (LSPD) experiment, and ultraviolet (UV) and mass spectroscopic analyses, in comparison with the data for **5c**. Further, treatment of **2b** with *p*-toluenesulfonic acid caused the same rearrangement reaction except that no demethylation occurred. On the other hand, (−)-dehydrogriseofulvin (**2d**) was recovered unchanged after similar treatment with the acid. However, under more vigorous conditions, **2d** was transformed into the racemic product.

Dienone–Phenol Rearrangement of 2′-Demethoxydehydrogriseofulvin on Treatment with Magnesium Iodide

(+)-2′-Demethoxydehydrogriseofulvin (**2b**) was prepared from (+)-griseofulvin (**1**) as described previously.[3] Since (−)-dehydrogriseofulvin (**2d**) was demethylated selectively with magnesium iodide[2b] to give 4-demethyldehydrogriseofulvin (**2c**), it was considered that the 4-methoxy group of (+)-2′-demethoxydehydrogriseofulvin (**2b**) would be demethylated under the same conditions as used for **2d**. The reaction of **2b** with magnesium iodide proceeded very smoothly, as compared with that of **2d**, to afford **3a**, mp 298—299 °C without recovery of the starting material. Compound **3a** was less polar than **2b** and on the basis of elemental analysis and mass (MS) spectrometry (M^+: *m/z* 306), the molecular formula was concluded to be $C_{15}H_{11}ClO_5$. Absorption maxima in the UV spectrum were observed at 240, 263, 307, and 387 nm, which are different from those of griseofulvin derivatives (**1**, **2a**—**c**, and **4c**). These data suggested that the product (**3a**) is neither a dehydrogriseofulvin not a benzophenone derivative but is a xanthone derivative formed by a dienone–phenol rearrangement. The structure of **3a** was determined by ^{13}C-NMR analysis of its acetyl derivative (**3b**).

Determination of the Structure of 3a

The acetylated compound (**3b**) was obtained as colorless needles, mp 249 °C. The MS and elemental analysis of **3b** gave the molecular formula $C_{19}H_{15}ClO_7$ and the circular dichroism (CD) spectrum could not be observed. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **3b** showed signals due to three methyl groups (2.32, 2.48, and 2.60 ppm), one

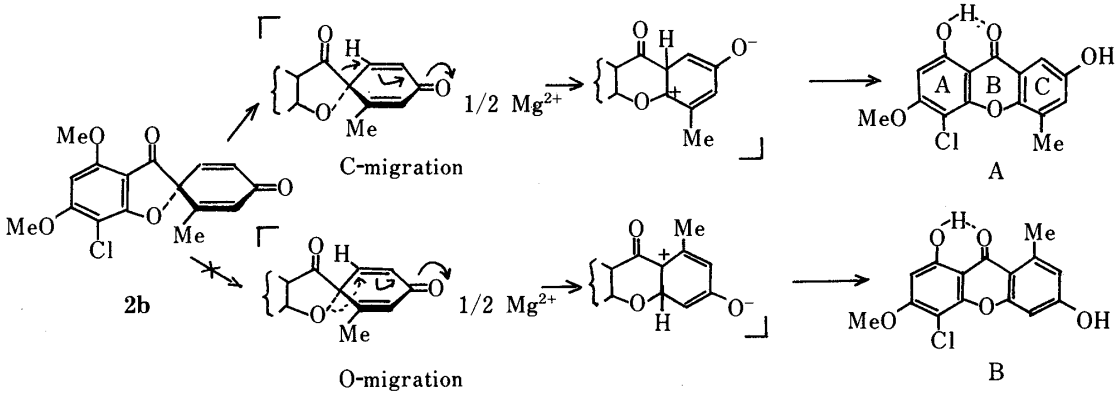
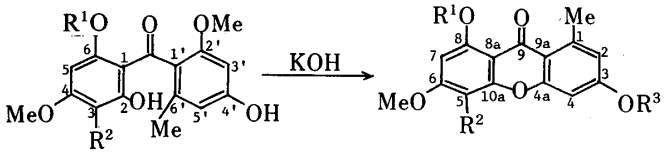


Chart 2

methoxy group (4.04 ppm), and three aromatic protons, suggesting that **3b** is a diacetylated xanthone derivative, A or B (Chart 2) which could be formed through C-migration or O-migration.

In order to determine the structure of **3a**, **5b** was synthesized as a standard sample from **4b** by a method similar to that used for the preparation of griseoxanthone C (**5a**)[4] from griseophenone C (**4a**) (Chart 3). The structure of the acetate (**5c**) was confirmed by a ^{13}C-NMR LSPD experiment.[5,6] The carbon chemical shifts and ^{13}C–^{1}H coupling constants for **5c**



4a: $R^1=R^2=H$ **5a**: $R^1=R^2=R^3=H$
4b: $R^1=Me$, $R^2=Cl$ **5b**: $R^1=Me$, $R^2=Cl$, $R^3=H$
4c: $R^1=H$, $R^2=Cl$ **5c**: $R^1=Me$, $R^2=Cl$, $R^3=COMe$

Chart 3

TABLE I. ^{13}C-NMR and LSPD Experiments: Assignments and Coupling Constants for 3-Acetoxy-5-chloro-6,8-dimethoxy-1-methylxanthone (**5c**)

Carbon	δ (ppm)	LSPD with NOE							Coupling constants (Hz)
		3-OCOCH$_3$	1-CH$_3$	OCH$_3$ 6-	OCH$_3$ 8-	7-H	2-H	4-H / 2-H[a] / 4-H[a]	
C-9	176.8 (br s)		s						
3-OCOCH$_3$	168.6 (q)	s							$^2J_{CH}=7.3$
C-6	160.4 (m)			d	d	q			$^2J_{CH}=3.7$, 4.6
C-8	159.7 (m)			d	d	q			$^2J_{CH}=3.7$, 4.6
C-4a	156.8 (d)							s / s	$^2J_{CH}=4.6$
C-10a	153.6 (s)								
C-3	153.5 (dd)						d	d / s	$^2J_{CH}=3.7$, 5.5
C-1	143.9 (q)		s						$^2J_{CH}=6.4$
C-2	120.9 (dm)		dd					dq	$^1J_{CH}=164.0$, $^3J_{CH}=2.8$, 5.5
C-9a	118.8 (m)		dd					q	$^3J_{CH}=2.8$, 3.7, 7.3
C-4	108.5 (dd)						d		$^1J_{CH}=168.6$, $^3J_{CH}=4.6$
C-8a	108.4 (d)					s			$^3J_{CH}=5.5$
C-5	101.3 (d)					s			$^3J_{CH}=7.3$
C-7	91.2 (d)								$^1J_{CH}=160.4$
6-OCH$_3$	56.5 (q)								$^1J_{CH}=145.7$
8-OCH$_3$	56.4 (q)								$^1J_{CH}=145.7$
1-CH$_3$	23.5 (dq)						q	q	$^1J_{CH}=129.2$, $^3J_{CH}=5.5$
3-OCOCH$_3$	21.1 (q)								$^1J_{CH}=130.1$

a) Since the signals due to 2- and 4-H were at 6.86 and 7.19 ppm, the variation of signals on irradiation at 7.0 ppm is described.

are summarized in Table I.

Next, the structure of **3b** was analyzed by means of a ^{13}C-NMR LSPD experiment. The carbon chemical shifts and ^{13}C–^{1}H coupling constants for **3b** are summarized in Table II. The data indicated unequivocally that **3b** is 5-chloro-2,8-diacetoxy-6-methoxy-4-methylxanthone.

This result clearly indicates that treatment of **2b** with magnesium iodide affords 5-chloro-2,8-dihydroxy-6-methoxy-4-methylxanthone (**3a**) by demethylation of the 4-methoxy group accompanied by a dienone–phenol rearrangement involving C-migration[7] of the grisan skeleton (Chart 2).

Consequently, in order to examine the effect of acids, (+)-2′-demethoxydehydrogriseofulvin (**2b**) was heated with *p*-toluenesulfonic acid in dry benzene for 20 min. The product (**6a**) was acetylated to give 2-acetoxy-5-chloro-6,8-dimethoxy-4-methylxanthone (**6b**). On the other hand, treatment of (−)-dehydrogriseofulvin (**2d**) with *p*-toluenesulfonic acid in dry benzene under the same conditions as described above resulted in the recovery of the starting material. However, **2d** afforded a racemic product (±)-**2d** in the presence of five times more *p*-toluenesulfonic acid. Compound **2d** did not suffer dienone–phenol rearran-

TABLE II. ^{13}C-NMR and LSPD Experiments: Assignments and Coupling Constants for 5-Chloro-2,8-diacetoxy-6-methoxy-4-methylxanthone (**3b**)

Carbon	δ (ppm)	LSPD with NOE							Coupling constants (Hz)
		$OCOCH_3$ 2-	$OCOCH_3$ 8-	$4\text{-}CH_3$	$6\text{-}OCH_3$	7-H	3-H	1-H	1-H[a] 3-H[a]	
C-9	174.5 (d)							s		$^3J_{CH}=4.6$
$8\text{-}O\underline{C}OCH_3$	169.4 (q)		s							$^2J_{CH}=6.4$
$2\text{-}O\underline{C}OCH_3$	169.3 (q)	s								$^2J_{CH}=6.4$
C-6	159.8 (m)				d	q				$^2J_{CH}=2.8, 4.6$
C-10a	153.5 (s)									
C-4a	151.3 (m)			dd			dq	dq	q	$^3J_{CH}=3.7, 8.3, 9.2$
C-8	149.8 (d)					s				$^2J_{CH}=5.5$
C-2	146.5 (dd)						d		s	$^2J_{CH}=3.7, 4.6$
C-3	129.5 (dm)			dd				dq		$^1J_{CH}=162.2, ^3J_{CH}=5.5, 5.5$
C-4	129.3 (q)			s						$^2J_{CH}=6.4$
C-9a	122.2 (s)									
C-1	116.0 (dd)						d			$^1J_{CH}=168.6, ^3J_{CH}=5.5$
C-8a	109.3 (d)									$^3J_{CH}=5.5$
C-5	108.0 (d)									$^3J_{CH}=7.3$
C-7	103.5 (d)									$^1J_{CH}=165.0$
$6\text{-}OCH_3$	56.9 (q)									$^1J_{CH}=145.7$
$8\text{-}OCO\underline{C}H_3$	21.2 (q)									$^1J_{CH}=130.1$
$2\text{-}OCO\underline{C}H_3$	21.0 (q)									$^1J_{CH}=130.1$
$4\text{-}CH_3$	15.6 (dq)						q		q	$^1J_{CH}=128.8, ^3J_{CH}=4.6$

a) Since the signals due to 1- and 3-H were at 7.75 and 7.31 ppm, the variation of signals on irradiation at 7.5 ppm is described.

gement on treatment with magnesium iodide. The present study thus demonstrated that the dienone–phenol rearrangement with magnesium iodide or *p*-toluenesulfonic acid occurs in dehydrogriseofulvin derivatives having no 2′-substituent.

Experimental

All melting points were obtained on a Shimadzu MM2 micro-melting point apparatus and are uncorrected. ^{1}H-NMR spectra were obtained at 270 MHz on a JEOL JNM-GX 270 FT NMR spectrometer. All ^{1}H-NMR data were recorded in deuteriochloroform and are reported as parts per million downfield from Me_4Si ($\delta=0$). ^{13}C-NMR spectra were determined at 67.8 MHz using a JEOL JNM-GX 270 FT NMR spectrometer with 32 K data points for acquisition of free induction decays. For measurements on carbon–proton coupling constants, the coupling information was retained using a gated decoupling facility which permitted retention of the nuclear Overhauser enhancement (NOE). The ^{13}C-NMR spectra for xanthone derivatives were obtained in deuteriochloroform. Spectra were referenced to the solvent signal, known separations from Me_4Si being employed in order to present chemical shift data in the conventional manner. Abbreviations used: s=singlet, d=doublet, br=broad, m=multiplet, dd=doublet of doublets, q=quartet. MS were recorded on a JEOL D-100 spectrometer at 75 eV ionizing potential. Column chromatography was performed with Kanto Kagaku silica gel (100 mesh). CD spectra were taken in a 1.5-mm cell at room temperature (24—25 °C) in chloroform on a JASCO J-20 recording spectropolarimeter, and were recorded (4 accumulations) from 380—230 nm.

Standard Samples——Syntheses and physico-chemical data except for UV data of griseophenone B (**4c**),[1b,8] 4-demethyldehydrogriseofulvin (**2c**),[2b] (−)-dehydrogriseofulvin (**2d**),[9] and (+)-2′-demethoxydehydrogriseofulvin (**2b**)[3] were described in the previous paper. **4c**: UV λ_{max}^{MeOH} nm (ε): 208 (39590), 294 (18570), 342 (5340). **2c**: UV λ_{max}^{MeOH} nm (ε): 216 (29140), 290 (32410). **2d**: UV λ_{max}^{MeOH} nm (ε): 214 (27810), 292 (29980). **2b**: UV λ_{max}^{MeOH} nm (ε): 214 (32210), 294 (27000).

5-Chloro-2,8-dihydroxy-6-methoxy-4-methylxanthone (3a)——A solution of magnesium iodide ether solvate (1.5 ml), prepared from magnesium turnings (390 mg) and iodine (1.9 g) in dry ether (24 ml) and dry benzene (4.8 ml), was filtered to remove the excess of magnesium and the filtrate was added dropwise to a stirred suspension of (+)-2′-demethoxydehydrogriseofulvin (**2b**) (270 mg) in dry benzene (20 ml). The mixture was stirred and refluxed for 20 min,

then, after cooling, poured into ice and water, and extracted with ethyl acetate. The ethyl acetate extract was washed with water, dried (Na_2SO_4) and concentrated *in vacuo*. Recrystallization of the residue (245 mg) from ethyl acetate gave **3a** as yellow needles, mp 298—299 °C. *Anal.* Calcd for $C_{15}H_{11}ClO_5$: C, 58.74; H, 3.62. Found: C, 58.63; H, 3.76. UV λ_{max}^{MeOH} nm (ε): 262 (36860), 307 (9650), 382 (5870). MS *m/z*: 306 (M^+) (for ^{35}Cl-compound) (base peak), 242.

Acetylation of 3a——A mixture of **3a** (100 mg), pyridine (1 ml) and Ac_2O (1 ml) was left to stand at room temperature overnight. The reaction mixture was poured into ice and water and extracted with chloroform. The chloroform extract was washed with water, dried (Na_2SO_4) and concentrated *in vacuo*. The residue (108 mg) was chromatographed on silica gel (30 g) and eluted with benzene–methylene chloride (40 : 60). The residue from the eluate, after recrystallization from methanol, gave **3b** as colorless needles, mp 249 °C. *Anal.* Calcd for $C_{19}H_{15}ClO_7$: C, 58.40; H, 3.87. Found: C, 59.04; H, 3.87. UV λ_{max}^{MeOH} nm (ε): 246 (49410), 300 (13550), 342 (5760). MS *m/z*: 390 (M^+) (for ^{35}Cl-compound), 348, 306 (base peak). ^{1}H-NMR δ (ppm): 2.32 (3H, s, 2-OCOCH$_3$), 2.48 (3H, s, 8-OCOCH$_3$), 2.60 (3H, s, 4-CH$_3$), 4.04 (3H, s, 6-OCH$_3$), 6.70 (1H, s, 7-H), 7.31 (1H, dd, J=2.8 Hz, 3-H), 7.75 (1H, m, J=2.9 Hz, 1-H). ^{13}C-NMR data are listed in Table I. The molecular ellipticity [θ] (c=1.0 mg/ml) was not observed in the region from 380 to 230 nm.

3-Acetoxy-5-chloro-6,8-dimethoxy-1-methylxanthone (5c)——A solution of 3-chloro-2,2′-dihydroxy-6′-methyl-2′,4,6-trimethoxybenzophenone (**4b**) (1.2 g) in 3 N KOH (60 ml) was refluxed under a nitrogen atmosphere for 36 h. The reaction mixture was cooled, acidified and extracted with ethyl acetate. Evaporation of the solvent yielded a yellow solid (1.1 g). The crude **5b** was chromatographed on silica gel (80 g) and eluted with benzene–methylene chloride (20 : 80). A mixture of **5b** (200 mg), pyridine (1.5 ml), and Ac_2O (1.5 ml) was left to stand at room temperature overnight, poured into ice and water, and extracted with chloroform. The chloroform extract was washed with water, dried (Na_2SO_4) and concentrated *in vacuo*. The residue (192 mg) was chromatographed on silica gel (40 g) and eluted with benzene–methylene chloride (40 : 60). The residue from the eluate, after recrystallization from chloroform, gave **5c** as pale yellow needles, mp 228—229 °C. *Anal.* Calcd for $C_{18}H_{15}ClO_6$: C, 59.59; H, 4.17. Found: C, 59.26; H, 4.34. UV λ_{max}^{MeOH} nm (ε): 242 (36690), 302 (16540), 334 (7770). MS *m/z*: 362 (M^+) (for ^{35}Cl-compound), 320 (base peak), 292. ^{1}H-NMR δ (ppm): 2.34 (3H, s, 3-OCOCH$_3$), 2.89 (3H, s, 1-CH$_3$), 4.04 (6H, s, 6- and 8-OCH$_3$), 6.42 (1H, s, 7-H), 6.86 (1H, dm, J=2.4, 0.7 Hz, 2-H), 7.19 (1H, dd, J=2.4, 0.7 Hz, 4-H). ^{13}C-NMR data are listed in Table II.

2-Acetoxy-5-chloro-6,8-dimethoxy-4-methylxanthone (6b)——A solution of **2b** (70 mg) and *p*-toluenesulfonic acid (3.5 mg) in dry benzene (14 ml) was heated under reflux. The solution was cooled and the yellow precipitate was collected by filtration. A mixture of the product (**6a**) (60 mg), pyridine (3 ml) and Ac_2O (3 ml) was left to stand at room temperature overnight, poured into ice and water, and extracted with chloroform. The chloroform extract was washed with 1% HCl, 5% Na_2CO_3 and water, dried (Na_2SO_4) and concentrated *in vacuo*. The residue (64 mg) was chromatographed on silica gel (20 g) and eluted with benzene–methylene chloride (50 : 50). The residue from the eluate, after recrystallization from methanol, gave **6b** as colorless needles, mp 232—233 °C. *Anal.* Calcd for $C_{18}H_{15}ClO_6$: C, 59.59; H, 4.17. Found: C, 59.20; H, 4.15. UV λ_{max}^{MeOH} nm (ε): 246 (40220), 306 (15040), 348 (7350). MS *m/z*: 362 (M^+) (for ^{35}Cl-compound), 303 (base peak). ^{1}H-NMR δ (ppm): 2.33 (3H, s, 2-OCOCH$_3$), 2.58 (3H, s, 4-CH$_3$), 4.04 (6H, s, 6- and 8-OCH$_3$), 6.44 (1H, s, 7-H), 7.28 (1H, m, 3-H), 7.78 (1H, dd, J=3.0, 0.7 Hz, 1-H). ^{13}C-NMR (in $CDCl_3$) δ (ppm): 15.6 (dq, $^1J_{CH}$=128.8 Hz, $^3J_{CH}$=4.6 Hz, 4-CH$_3$), 21.1 (q, $^1J_{CH}$=130.1 Hz, 2-OCOCH$_3$), 56.6 (q, $^1J_{CH}$=145.7 Hz, 6- and 8-OCH$_3$), 91.2 (d, $^1J_{CH}$=160.4 Hz, C-7), 102.0 (d, $^3J_{CH}$=7.3 Hz, C-5), 107.1 (d, $^3J_{CH}$=6.4 Hz, C-9a), 116.0 (dd, $^1J_{CH}$=168.2 Hz, $^3J_{CH}$=5.5 Hz, C-9), 123.0 (s, C-8a), 128.8 (dm, $^1J_{CH}$=162.2 Hz, $^3J_{CH}$=5.5, 5.5 Hz, C-3), 129.0 (q, $^2J_{CH}$=6.4 Hz, C-4), 146.4 (dd, $^2J_{CH}$=3.7, 4.6 Hz, C-2), 150.8 (m, $^3J_{CH}$=3.7, 8.2, 9.2 Hz, C-4a), 154.1 (s, C-10a), 160.1 (m, $^2J_{CH}$=3.7 Hz, C-8), 160.5 (m, $^2J_{CH}$=3.7 Hz, C-6), 169.5 (q, $^2J_{CH}$=7.3 Hz, 2-OCOCH$_3$), 174.8 (d, $^3J_{CH}$=3.7 Hz, C-9).

(±)-Dehydrogriseofulvin ((±)-2c)——A solution of (−)-dehydrogriseofulvin (**2d**) (100 mg) and *p*-toluenesulfonic acid (25 mg) in dry benzene (20 ml) was heated under reflux. The solution was cooled and extracted with benzene. The benzene extract was washed with 2 N Na_2CO_3 and water, dried (Na_2SO_4) and concentrated *in vacuo*. The residue (92 mg) was chromatographed on silica gel (30 g) and eluted with benzene–methylene chloride (30 : 70). The eluate gave colorless needles, (±)-dehydrogriseofulvin ((±)-**2d**), mp 290—291 °C (dec.), $[\alpha]_D^{25}$ 0° (c=0.25, acetone). ^{1}H-NMR and MS; identical with those of (−)-dehydrogriseofulvin (**2d**).[9]

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