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^{13}C NMR Signal Assignments of Herqueinone and Its Phenalenone Derivatives

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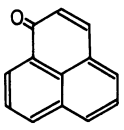
The full assignments of the ^{13}C NMR signals of the herqueinone-type phenalenone, herqueinone, were established by a combination of the single-frequency off-resonance decoupling technique and the ^{13}C-enrichment technique using the ^{13}C-labeled tracer. Furthermore, the full assignments of the ^{13}C NMR signals of deoxyherqueinone-type, dihydroherqueinone-type, and xanthoherqueinone-type phenalenone were completed on the basis of the application of the chemical shift rule and the mutual comparison of their chemical shifts.

The red pigments of *Penicillium herquei*,[1-3] such as herqueinone (**2**), atrovenetin (**4**), and deoxyherqueinone (**5**), are compounds having a phenalenone skeleton (**1**) and a 1,2,2-trimethyltetrahydrofuran ring.†,[3-14]

The biosynthetic mechanism for the formation of the phenalenone skeleton of deoxyherqueinone (**5**) was clarified by feeding experiments with ^{14}C- and ^{13}C-labeled acetates.[15-18] On the other hand, the feeding experiment of ^{13}C-labeled malonate indicated that the trimethylfuran ring of herqueinone-type pigments was biologically formed from mevalonic acid.[17,18] However, a biosynthetic mechanism for the formation of the trimethylfuran ring fused to the phenalenone skeleton is still unknown. Before clarifying the mechanisms of the prenylation and the cyclization of its prenyl chain, it was necessary to complete the full assignments of the ^{13}C NMR signals of herqueinone (**2**) and its derivatives (**3**) and (**5**)—(**13**). We have now established the full assignments of the ^{13}C NMR signals of these phenalenones by use of the decoupling techniques and the ^{13}C-enrichment technique.



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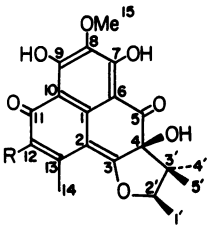
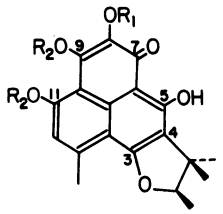
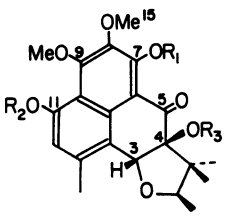


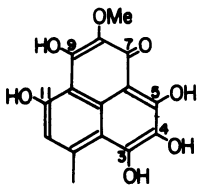
2: R=H
3: R=Br



4: R_1=R_2=H
5: R_1=Me, R_2=H
6: R_1=R_2=Me
7: R_1=Me, R_2=COMe



8: R_1=R_2=R_3=H
9: R_1=R_2=COMe, R_3=H
10: R_1=Me, R_2=R_3=H
11: R_1=Me, R_2=COMe, R_3=H
12: R_1=Me, R_2=R_3=COMe



13

† This is abbreviated as trimethylfuran ring hereinafter.

Results and Discussion

The phenalenones derived from herqueinone (**2**) were classified into four groups, such as herquinone-type, deoxyherqueinone-type, dihydroherqueinone-type, and xanthoherqueinone-type phenalenones, on the ground of their structures. The assignments of the ^{13}C NMR signals of these four types of phenalenones were completed as follows.

Herqueinone-type Phenalenones. The proton noise decoupling ^{13}C NMR spectra of herqueinone (**2**) exhibited 20 signals in [$^2H_6$]dimethyl sulfoxide and [$^2H_5$]pyridine solutions. The signals at δ_c 131.3, 109.2, 178.6, 78.9, 150.7, and 138.8 were assigned to C-1, C-2, C-3, C-4, C-8, and C-13, respectively, on the basis of the application of the chemical shift rule[19,20] and the comparison of the ^{13}C chemical shifts of **2** with those of the corresponding carbon atoms of previously reported deoxyherqueinone diacetate (**7**).[17,18] Furthermore, the ^{13}C NMR signals due to the protonated carbon atoms at the 12-, 14-, 15-, 1′-, 2′-, 4′-, and 5′-positions were completely assigned by use of Birdsall's method,[21] as shown in Fig. 1. Consequently, the signals at δ_c 122.8, 59.9, 18.6, 95.9, and 15.9 were assigned to C-12, C-15,

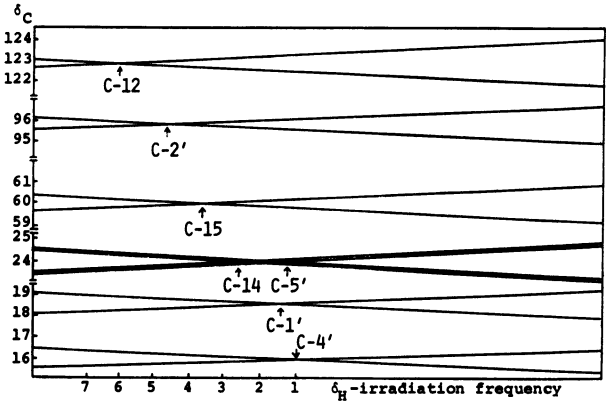


Fig. 1. Birdsall plot of SFORD data for herqueinone (**2**).

C-1′, C-2′, and C-4′, respectively. The signals of C-5′ and C-14 overlapped each other at δ_c 23.8. On the other hand, the distinction between the signals for C-5 and C-11, C-6 and C-10, and C-7 and C-9 was difficult, because of the symmetry of the phenalenone skeleton. However, we succeeded in full assignments of these signals as follows. First, the assignments of the signals due to C-6 and C-10 were completed by the gated decoupling method; the spectrum in the presence of D_2O exhibited $^3J_{CH}$ (4 Hz) at δ_c 103.2 to the aromatic proton on C-12 and the singlet signal at δ_c 102.7, and the signals at δ_c 102.7 and 103.2 were evidently assigned to C-6 and C-10, respectively. Next, the distinction between the signals for C-5 and C-11 and C-7 and C-9, in addition to C-6 and C-10, at the symmetrical positions of the molecule was performed by diagnosis of the ^{13}C–^{13}C spin couplings due to the nine acetate units in the molecule of ^{13}C-enriched herqueinone (**2**) biosynthesized by incorporation of [1,2-$^{13}C_2$]acetate in *P. herquei*. As the incorporation pattern of seven acetate units in the phenalenone skeleton of deoxyherqueinone (**5**) biosynthesized from [1,2-$^{13}C_2$]acetate in *P. herquei* has been previously established,[17,18] the carbon skeleton of the molecule of herqueinone (**2**) should be occupied by the ^{13}C–^{13}C spin coupling pairs originating from [1,2-$^{13}C_2$]acetate as shown in Fig. 2. The ^{13}C NMR spectra of the ^{13}C-enriched herqueinone (**2**) showed the nine ^{13}C–^{13}C spin couplings as shown in Table 1. Analysis of the coupling constants established the assignments of the signals for C-5, C-6, C-9, C-10, and C-11 which constituted the coupling pairs with C-4, C-7, C-8, C-1, and C-12, respectively Thus, the full assignments of the ^{13}C NMR signals of herqueinone (**2**) were completed.

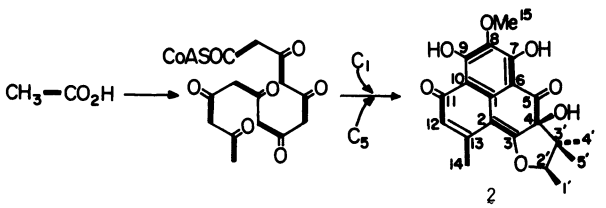


Fig. 2. ^{13}C incorporation pattern of the acetate units (—) in herqueinone (**2**).

TABLE 1. ^{13}C–^{13}C SPIN COUPLINGS IN THE ^{13}C NMR SPECTRUM OF HERQUEINONE (2) BIOSYNTHESIZED FROM [1,2-$^{13}C_2$]ACETATE[a]

Carbon	δ_C[b]	$^1J_{CC}$	Carbon	δ_C[b]	$^1J_{CC}$
1	131.3	80	11	186.4	56
2	109.2	75	12	122.8	58
3	178.6	75	13	138.8	35
4	78.9	51	14	23.8	35
5	197.0	51	15	59.9	0
6	102.7	61	1′	18.6	38
7	162.0	61	2′	95.9	38
8	150.7	42	3′	43.1	36[c]
9	163.0	44	4′	15.9	37
10	103.2	79	5′	23.8	0

a) These δ_C and $^1J_{CC}$ values differ from those described in Ref. 7, but these are the corrected after careful reexamination. b) Taken in [$^2H_6$]DMSO containing TMS as an internal standard (δ_{TMS}=0.0) : number of scan; 29253 times. c) These $^1J_{CC}$ values were obtained in [$^2H_5$]pyridine.

The chemical shifts of the ^{13}C NMR signals of bromoherqueinone (**3**) were in fair agreement with those of **2** except for that of the conjugated carbonyl group at the 11-position. The C-11 signal of **3** shifted to higher-field by about 5 ppm in comparison with that of **2**. This higher-field shift might be caused by the reason why the halogenation at the neighboring position of the conjugated carbonyl group breaks up slightly the conjugated system. Such a higher-field shift has been observed on the ^{13}C NMR spectrum of 3-bromo-5-hydroxy-1,4-naphthoquinone.[22]

Deoxyherqueinone-type Phenalenones. Deoxygenation at the 4-position of herqueinone (**2**) gave deoxyherqueinone (**5**), which was then converted into the corresponding dimethyl ether (**6**) and diacetate (**7**). The ^{13}C chemical shifts of the diacetate (**7**) were in fair agreement with those of the deoxyherqueinone diacetate described previously in the literature.[17,18] These described chemical shifts were supported by examination of the assignments of the protonated carbon atom signals by use of Birdsall's method.[21] For the signals at δ_C 163.5 and 159.6 in the ^{13}C NMR spectrum of **5**, these were assigned to C-9 and C-11, respectively, by considering the acetylation shift between the signals of **5** and **7**. The signals of C-9 and C-11 overlapped at δ_c 161.5 in the ^{13}C NMR spectrum of **6**. The assignments of the other ^{13}C NMR signals of **5** and **6** were completed by comparing the signals with those of the corresponding carbon atoms of **7**.

Dihydroherqueinone-type Phenalenones. Herqueinone (**2**), on hydrogenation followed by methylation, gave dihydroherqueinone monomethyl ether (**8**) and dimethyl ether (**10**). Acetylation of **8** afforded the diacetate (**9**) with two acetoxyl groups at the 7- and 11-positions. On the other hand, acetylation of **10** gave the monoacetate (**11**) with an acetoxyl group at the 11-position and diacetate (**12**) with two acetoxyl groups at the 4- and 11-positions.

The ^{13}C NMR signal of C-3 of these dihydroherqueinone-type phenalenones (**8**—**12**) was assigned by use of the off-resonance decoupling technique. The signals of C-9 and C-11 of **8** were assigned on the basis of the higher-field shift of about 10 and 30 ppm, respectively, in comparison with those of **2**. The other signals of **8** were assigned by comparison of the chemical shifts with those of the corresponding carbon atoms of **2**. On the other hand, the assignments of the signals for C-7 of **9**—**12** and for C-11 of **9**, **11**, and **12** were completed on the basis of the higher-field shifting on methylation or acetylation. The other ^{13}C signals of dihydroherqueinones (**9**—**12**) were assigned by comparison of the chemical shifts with those of the corresponding carbon atoms of **2** and **8**.

It is interesting to note that the ^{13}C NMR signal of C-1′ of deoxyherqueinones (**5**—**7**) and the signal of C-5′ of dihydroherqueinones (**8**—**12**) appear at a higher field in comparison with those of the corresponding carbon atoms of herqueinone (**2**), while the signals of C-4′ and C-5′ of deoxyherqueinones (**5**—**7**) appear

TABLE 2. ^{13}C NMR CHEMICAL SHIFTS (δ_C)[a] FOR HERQUEINONE (2) AND ITS DERIVATIVES (3) AND (5—13)

Carbon	2	3[b]	5	6	7	8	9	10	11	12	13
1	131.3	132.4	126.2	126.4	125.3	129.1	129.7	130.8	131.4	130.3	120.4
2	109.2	109.7	107.1	108.9	113.6	117.8	127.4	112.7	127.1	127.2	111.0
3	178.6	179.5	164.7	166.6	175.1	81.5	82.5	82.2	83.6	81.9	152.3
4	78.9	80.4	118.2	118.7	121.0	82.0	83.5	84.3	85.2	88.4	130.1
5	197.0	197.6	170.0	172.9	175.7	202.9	197.2	199.0	199.8	190.8	165.4
6	102.7	103.2	104.7	107.3	108.9	105.9	117.1	118.6	117.3	116.9	103.2
7	162.0	163.1	171.4	175.1	175.7	162.0	143.2	153.2	155.6	155.8	170.4
8	150.7	149.0	145.1	145.1	143.5	140.2	144.8	142.4	145.2	144.9	145.2
9	163.0	163.1	163.5	161.5	149.9	153.9	152.2	153.2	153.4	152.6	160.2
10	103.2	104.4	104.7	108.3	108.9	109.2	118.1	119.3	118.4	118.7	104.3
11	186.4	180.5	159.6	161.5	143.5	156.6	145.4	154.9	145.0	144.9	158.3
12	122.8	121.9	115.8	111.3	122.9	113.5	124.1	113.6	123.6	123.1	115.9
13	138.8	138.1	133.1	141.4	143.5	136.5	138.1	138.5	138.3	136.5	132.7
14	23.8	22.3	23.2	23.4	23.4	24.6	23.6	23.2	24.5	23.9	25.0
15	59.9	60.3	59.8	60.3	60.4	60.9	61.2	61.1	61.3	61.0	59.9
7-OCH_3								61.8	62.1	61.6	
9-OCH_3				61.3		62.4	61.9	62.4	62.1	61.9	
11-OCH_3				56.6							
4-$OCOCH_3$										20.6	
										170.0[c]	
7-$OCOCH_3$							20.4				
							169.4[c]				
9-$OCOCH_3$					20.6[c]						
					167.9[d]						
11-$OCOCH_3$					21.0[c]		20.4		20.9	20.6	
					168.9[d]		168.0[c]		169.8	169.4[c]	
1′	18.6	19.0	14.3	14.3	14.6	17.6	17.8	18.1	18.0	17.9	
2′	95.9	97.0	90.6	91.1	92.0	81.5	81.8	82.2	83.0	81.7	
3′	43.1	43.8	42.8	42.7	43.5	50.1	50.3	50.2	51.9	50.2	
4′	15.9	16.4	20.4	20.3	20.5	16.3	15.8	15.6	15.8	15.0	
5′	23.8	22.3	25.3	25.3	25.7	19.9	19.3	19.4	20.0	19.2	

a) Taken in [$^2H_6$]DMSO (δ_{TMS}=0.0): number of scan; *ca.* 1500—4300 times. b) Taken in [$^2H_5$]pyridine. c and d) Values in any vertical column may be interchanged although those given here are preferred.

at a lower field in comparison with those of **2**. These seem to be due to the difference in the influence of the anisotropy[23] caused by the phenalenone ring. The plane angle formed by the phenalenone skeleton and the trimethylfuran ring of the deoxyherqueinones (**5**—**7**) is about 180° in model.[24] Therefore, the anisotropic effect to the C-1′ methyl group of deoxyherqueinones (**5**—**7**) may be greater than that in the case of herqueinone (**2**), whereas the effect to the C-4′ and C-5′ methyl groups may be less than that in that case. On the other hand, the plane angle of dihydroherqueinones (**8**—**12**), is smaller than that in the case of herqueinone (**2**). Therefore, the C-4′ and C-5′ methyl groups of **8**—**12** may be equally influenced by the anisotropy of the carbonyl group and the aromatic rings.

Xanthoherqueinone-type Phenalenone. The ^{13}C NMR chemical shifts of xanthoherqueinone (**13**) were in fair agreement with those of the phenalenone skeleton of **5**, except for the signals of phenolic carbon atoms at the 3-, 4-, and 5-positions. These signals appeared at δ_C 152.3, 130.1, and 165.4 and were assigned to the phenolic carbon atoms, respectively, by application of the chemical shift rule.

The final assignments of the ^{13}C NMR signals of herqueinone (**2**) and its derivatives (**3**) and (**5**—**13**) are given in Table 2.

Experimental

The fungal culture of *Penicillium herquei* Bainer and Sartory (IFO 7904) was obtained from the Institute for Fermentation.†† Sodium [1,2-$^{13}C_2$]acetate was purchased from the British Oxygen Company Co. Ltd. The ^{1}H NMR spectra were taken, with TMS as an internal standard, at 60 and 90 MHz. The ^{13}C NMR spectra were obtained on a Hitachi R-42 FT NMR spectrometer at 22.631 MHz at 35 °C in an 8 mm spinning tube; precisions of δ_c are about $\pm$0.1. FT measurement conditions were as follows: spectral width, 250 ppm; filtering, 6 KHz; pulse width, 45°; pulse interval, 1.800 s; number of data points, 8000. The series of single-frequency off-resonance decoupling ^{13}C NMR spectra of herqueinone (**2**) and deoxyherqueinone diacetate (**7**) were recorded with the ^{1}H decoupling frequency set at ten different points started from the upfield to the downfield in increments of about 100 Hz in the ^{1}H NMR region (Fig. 1). The gated decoupling with NOE was measured by a JEOL FX-200 FT NMR spectrometer at 50.150 MHz at 0 °C in a 5 mm spinning tube: pulse width, 45°; pulse interval, 6.00 s; number of data points, 8000; precisions of δ_C, $\pm$0.02. The EI-MS spectra were obtained on a Hitachi RMU-6L mass spectrometer at 70 eV. Analytical and preparative TLC were carried out on Merck 60 GF_{254} silica-gel plates which were 0.25- and 0.5 mm-thick, respectively.

Isolation of Herqueinone. The spores, obtained from the preculture of *P. herquei* on the malt extract-agar medium, were

†† Jyuso hon-machi, Yodogawa-ku, Osaka 532.

TABLE 3. PHYSICAL AND ANALYTICAL DATA OF PHENALENONE DERIVATIVES (3) AND (5—13)

Compound	Mp θ_m/°C	$[\alpha]_D^{25}$/° (c, $CHCl_3$)	Mol formula	Calcd (%)			Found (%)		
				C	H	Br	C	H	Br
3	234(decomp)[a]	+580(0.053)[b]	$C_{20}H_{19}O_7Br$	53.23	4.24	17.74	52.94	4.24	17.45
5	221—222[c]	+55.9(0.68)	$C_{20}H_{20}O_6$	67.40	5.66		67.64	5.55	
6	166—168[d]	+70.5(0.75)[e]	$C_{22}H_{24}O_6$	68.73	6.29		69.02	6.19	
7	174—175[f]	+52.5(3.20)[g]	$C_{24}H_{24}O_8$	65.44	5.49		65.24	5.57	
8	173—174[h]	+39.0(6.03)	$C_{21}H_{24}O_7$	64.93	6.23		64.65	6.33	
9	Gum	−13.7(2.05)	$C_{25}H_{28}O_9$	63.35	5.97		63.38	6.08	
10	151—155[i]	−18.5(7.28)	$C_{22}H_{26}O_7$	65.66	6.51		65.38	6.63	
11	Gum	−24.3(1.20)	$C_{24}H_{28}O_8$	64.85	6.35		64.78	6.35	
12	Gum	−123(1.35)	$C_{26}H_{30}O_9$	64.18	6.22		64.11	6.18	
13	288—290[j]		$C_{15}H_{12}O_7$	59.21	3.98		59.67	3.87	

a) Ref. 3; 235 °C(decomp). b) Ref. 3; $[\alpha]_D$+460°($CHCl_3$). c) Ref. 8; 225 °C. d) Ref. 8; 168—169 °C. e) Ref. 8; $[\alpha]_D$+76°($CHCl_3$). f) Ref. 3; 174—175 °C. g) Ref. 3; $[\alpha]_D$+57°($CHCl_3$). h) Ref. 8; 172—174 °C. i) Ref. 8; 151—154 °C. j) Ref. 2; 290—293 °C.

TABLE 4. SPECTRAL DATA OF PHENALENONE DERIVATIVES (3) AND (5—13)

Compound	IR (Nujol) ν_{max}/cm^{-1}
3	3356(OH), 1621(C=O), 1586 and 1507 (arom. C=C), 1235 and 1042(C-O-C), and 1098(cyclic C-O-C)
5	3265(OH), 1610(C=O), 1595 and 1490 (arom. C=C), 1280 and 1064(C-O-C), and 1097(cyclic C-O-C)
6	3450(OH), 1607(C=O), 1585 and 1500 (arom. C=C), 1262, 1221, 1058, 1033, and 1013(C-O-C), and 1102(cyclic C-O-C)
7	3350(OH), 1776 and 1174(2×$OCOCH_3$), 1617(C=O), 1594 and 1505(arom. C=C), 1227 and 1032(C-O-C), and 1100(cyclic C-O-C)
8	3460 and 3366(OH), 1632(C=O), 1609 and 1577(arom. C=C), 1258, 1217, 1041, and 1018(C-O-C), and 1093(cyclic C-O-C)
9	3490(OH), 1765, 1245, and 1180(2×$OCOCH_3$), 1668(C=O), 1615 and 1561 (arom. C=C), 1217, 1063, and 1023 (C-O-C), and 1100(cyclic C-O-C)
10	3445 and 3334(OH), 1672(C=O), 1628 and 1570(arom. C=C), 1276, 1214, 1063, and 1026(C-O-C), and 1113(cyclic C-O-C)
11	3491(OH), 1757, 1253, and 1173 ($OCOCH_3$), 1670(C=O), 1614 and 1562 (arom. C=C), 1213, 1027 and 1066 (C-O-C), and 1115(cyclic C-O-C)[a]
12	1763, 1735, 1243, and 1174(2×$OCOCH_3$), 1683(C=O), 1613 and 1558(arom. C=C), 1205, 1066, and 1046(C-O-C), and 1112 (cyclic C-O-C)[a]
13	3400(OH), 1700(C=O), 1600 and 1505 (arom. C=C), 1275 and 1030(C-O-C)

a) Taken in the neat film.

inoculated to the Raulin-Thom solution.[2] After inoculation, this culture of *P. herquei* was incubated at 25 °C for 25 d. The mycelia produced on the medium were filtered off, and immersed in EtOAc. On the other hand, the filtered medium was acidified to pH 5, and extracted with EtOAc. This EtOAc extract of the medium was combined with the EtOAc extract of the mycelia, because the two EtOAc extracts exhibited the same behavior on TLC. The combined EtOAc extract (*ca.* 5 g), after removal of the solvent, was subjected to centrifugal liquid chromatography on silica gel (3 mm in thickness and 10 cm in radius) with EtOAc–hexane (1 : 4 v/v) as solvent to give a red powder (310 mg). Recrystallization of this red powder from EtOH gave herqueinone (**2**) (275 mg) as red needles: mp 217—218 °C (lit,[8] 218—222 °C); $[\alpha]_D^{25}$ +374° (c 1.68, $CHCl_3$) (lit,[8] $[\alpha]_D$ +300° ($CHCl_3$)); IR (Nujol) 3300 (OH), 1640 and 1626 (C=O), 1591 and 1512 (aromatic C=C), 1247 and 1039 (C-O-C), and 1100 cm^{-1} (cyclic C-O-C); IR (0.0002M, CCl_4) 3315 cm^{-1} (intramolecular hydrogen bonded OH); UV_{max} (cyclohexane) 450 (log ε 4.45), 307 (5.60), 254 (5.08), and 223 nm (5.34); ^1H NMR ([$^2H_6$]DMSO) δ=6.28 (1H, d, J=1.5 Hz, 12-H), 4.83 (1H, q, J=6.5 Hz, 2′-H), 3.80 (3H, s, 15-H_3), 2.50 (3H, d, J=1.5 Hz, 14-H_3), 1.55 (3H, d, J=6.5 Hz, 1′-H_3), 1.40 (3H, s, 5′-H_3), and 1.00 (3H, s, 4′-H_3); MS m/z (rel intensity) 372 (M^+, 100%) and 341 (M^+-OCH_3, 68).

Found: C, 64.51; H, 5.49%. Calcd for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41%.

Preparation of ^{13}C-enriched Herqueinone. Sodium [1,2-$^{13}C_2$]acetate (270 mg, 92% enriched) dissolved in distilled water (5 ml) was added into each of 5 flasks which contained a 14-d old culture (200 ml) of *P. herquei*. After further cultivation for 11 d, the usual work-up of the cultures gave the sample of ^{13}C-enriched herqueinone (**2**) (44 mg), with about 31% ^{13}C-abundance at each labeled position. The ^{13}C–^{13}C spin couplings in the ^{13}C NMR spectra of the ^{13}C-enriched **2** were determined, and the results are given in Table 1.

Preparation of the Phenalenone Derivatives. According to the method givin in the literature,[3] bromoherqueinone (**3**) and deoxyherqueinones (**5**—**7**) were derived from herqueinone (**2**) as follows. Bromination of **2** with Br_2 gave bromoherqueinone (**3**). Deoxygenation of **2** with Zn dust gave deoxyherqueinone (**5**). Furthermore, **5** was methylated with CH_2N_2 to give the dimethyl ether (**6**), and acetylated with the acetic anhydride–pyridine mixture to give the diacetate (**7**). The dihydroxyherqueinones (**8**—**12**) were also derived from **2** following the method given in the literature[8] as follows. Methylation of the product, obtained by hydrogenation of **2** in the presence of Pd–C, gave dihydroherqueinone methyl ethers (**8**) and (**10**). These methyl ethers were acetylated with the acetic anhydride–pyridine mixture to give the acetates (**9**) and (**11**), and with the acetic anhydride–*p*-toluenesulfonic acid mixture to give the diacetate (**12**). Xanthoherqueinone (**13**) was derived from **2** by acid-hydrolysis under the same conditions as described in the literature.[2]

The physical and analytical data of these phenalenones (**3**)

Table 5. UV and MS spectral data of phenalenone derivatives (3) and (5—13)

Compound	UV(EtOH) λ_{max}/nm (log ϵ)	MS (70 eV) m/z (rel intensity)
3	450(4.09), 307(5.16), 255(5.42), and 230(5.65)[a]	452 (M^++2, 100) and 450 (M^+, 89)
5	407(4.24) and 370(4.15)	356 (M^+, 52) and 341 (M^+-CH_3, 100)
6	402(4.21) and 375(4.20)	384 (M^+, 46) and 369 (M^+-CH_3, 100)
7	433(5.15), 410(5.34), and 360(5.09)	440 (M^+, 28), 398 (26), and 356 (100)
8	402(3.90) and 357(3.74)	388 (M^+, 100) and 373 (M^+-CH_3, 6)
9	355(3.80) and 330(3.67)	472 (M^+, 30), 430 (21), 388 (57), and 301 (100)
10	388(3.55) and 375(3.58)	402 (M^+, 62), 387 (M^+-CH_3, 12), and 301 (100)
11	348(4.32) and 334(4.29)	444 (M^+, 34), 402 (14), and 316 (100)
12	350(4.07) and 334(4.02)	486 (M^+, 20), 426 (52), and 369 (100)
13	399(3.97) and 314(4.08)	

a) Taken in cyclohexane.

Table 6. ^1H NMR Spectral data[a] of phenalenone derivatives (3) and (5—13)

Compound	1′-H_3 (J/Hz)	4′-H_3	5′-H_3	14-H_3	$OCOCH_3$	OCH_3	2′-H (J/Hz)	3-H	12-H
3[b]	1.57d[c] (6.5)	1.00	1.38	2.77		3.78	4.90q[c] (6.5)		
5	1.48d (6.5)	1.32	1.57	2.82		4.09	4.64q (6.5)		6.83
6	1.47d (6.5)	1.33	1.57	2.88		4.01[d] 4.09	4.64q (6.5)		6.86
7	1.42d (6.5)	1.29	1.51	2.80	2.32 2.36	4.01	4.62q (6.5)		6.94
8	1.34d (6.5)	0.80	1.17	2.53		3.98 4.28	3.68q (6.5)	5.44	6.72
9	1.27d (6.5)	0.83	1.08	2.61	2.36 2.41	3.90 3.99	3.64q (6.5)	5.52	7.06
10	1.22d (6.5)	0.89	1.08	2.52		3.92 4.06 4.20	3.61q (6.5)	5.46	6.78
11	1.23d (6.5)	0.92	1.10	2.58	2.36	3.88 3.96 4.03	3.60q (6.5)	5.47	6.94
12	1.20d (6.5)	1.00	1.24	2.54	2.14 2.34	3.91 3.99 4.06	3.62q (6.5)	5.50	6.97
13[b]				2.63		3.79			6.54

a) Taken in [^2H]$CHCl_3$ containing TMS as an internal standard. b) Taken in [$^2H_6$]DMSO. c) d=doublet and q=quartet. d) Two methyl signals overlap.

and (5—13) are given in Table 3, and the spectral data of them are summarized in Tables 4—6.

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