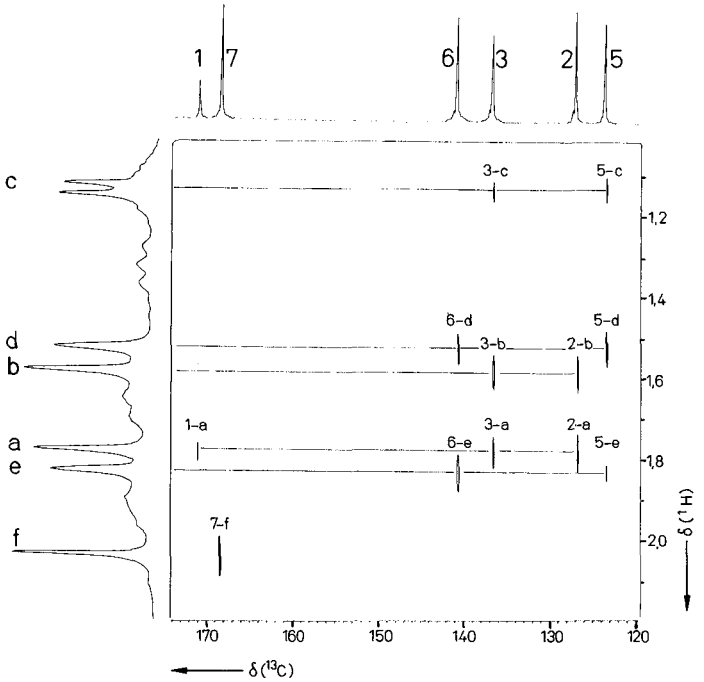

Fig. 2. Section of the H,C-COLOC spectrum of *rac*-**1** for the olefinic carbon atoms and the carbonyl groups, in the proton region of the methyl groups. Spectrometer: Bruker WH 270. Measuring conditions: 150 mg in 2 mL $CDCl_3/C_6D_6$ (5:1); $\Delta_1=\Delta_2=40$ ms; spectral width in $\omega_1=1850$ Hz, in $\omega_2=3625$ Hz. Total duration of a scan 1.5 s. 140 increments of 1 K with 192 scans each. Total recording time: 12 h. The phases of the 90°-^{1}H-pulse were cycled independently of one another in 90° steps with respect to the receiver phase ($\phi_1=k\times90°$, $\phi_{det}=-k\times90°$, $k=0, 1, 2, \ldots$ and $\phi_3=m\times90°$, $\phi_{det}=-m\times90°$, $m=0, 1, 2, \ldots$; $\phi_2=\phi_4=\phi_5=0$).

The spectrum of *rac*-**2** (Fig. 3) reveals the presence of two conformers in solution, of which the dominating one has the conformation determined in the crystal. This was proven by dissolution at −80 °C in CD_2Cl_2 and immediate ^{1}H-NMR measurements[9]. The conformation occurring on warming the solution is formed through steric hindrance of rotation about the single bond between C4 and C5[7]. The H,C-COLOC spectrum of the dominating conformation can be interpreted completely analogously to that of the isomeric *rac*-**1**.

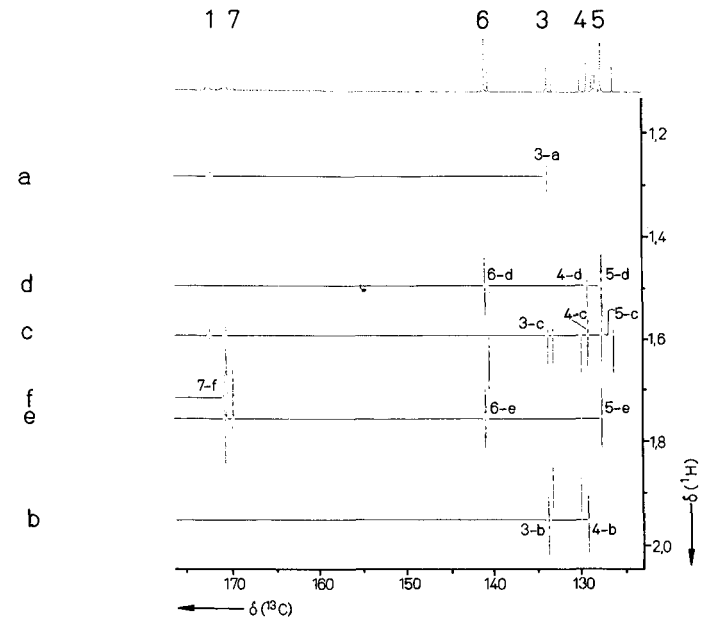

Fig. 3. Section of the H,C-COLOC spectrum of *rac*-**2**. Spectrometer: Bruker AM 500. Measuring conditions: 240 mg in 2 mL C_6D_6. $\Delta_1=60$ ms, $\Delta_2=40$ ms; spectral width in $\omega_1=3800$ Hz, in $\omega_2=6670$ Hz. Total duration per scan 1.5 s. 180 increments of 4 K with 128 scans each. Total recording time: 10 h. Other than for the spectrum in Figure 2, the phase of the 90°-^{13}C-pulse was also cycled with respect to the receiver phase ($\phi_5=n\times90°$, $\phi_{det}=n\times90°$, $n=0, 1, 2, \ldots$; $\phi_2=\phi_4=0$). This led to a better suppression of spectral artefacts.

The method presented here, which employs H,C-couplings via two and three bonds, can be used with advantage for the assignment of quaternary carbon atoms, whose environment is thus also determinable. For its application to aliphatic carbon atoms we recommend the use of a low-pass J filter[10] for suppressing the direct C–H cross signals[11]. The new pulse sequence enables a convenient and, other than the conventional H,C-COSY sequence, effective optimization of the delay for the whole experiment. It is especially suitable, therefore, for the investigation of complex molecules, where intensity maximization is of importance due to scarcity of substance or short relaxation times.

The sensitivity of the experiment described here, like that in the relayed H,C-COSY technique, can be rated between that of H,C-COSY and 2D-INADEQUATE.

Received: February 24, 1984;
revised: March 22, 1984 [Z 722 IE]
German version: *Angew. Chem. 96* (1984) 434

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Pigments from the Cap Cuticle of the Bay Boletus *(Xerocomus badius)***

By *Bert Steffan* and *Wolfgang Steglich**

Dedicated to Professor Sir Derek Barton on the occasion of his 65th birthday

The bay boletus [*Xerocomus badius* (Fr.) Kühn. ex Gilb.], highly prized as an edible fungus, has a chocolate-brown pileus. The pigments contained therein are apparently present in the form of salts, since addition of a small amount of hydrochloric acid is necessary for their extrac-

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[**] Fungal Pigments, Part 44. This work was supported by the Deutsche Forschungsgemeinschaft. We thank Dr. *M. Schmitz*, Bonn, for recording the X-ray emission spectra and Dr. *G. Wolf*, Bruker, Karlsruhe for high-field NMR measurements.—Part 43: W. Steglich, B. Oertel, *Sydowia Ann. Mycol.*, in press.

tion with methanol-acetone. The separation and purification of the pigments can be achieved by multiple chromatography on Sephadex LH20 with methanol as eluent; besides the main products badion A **2a** and norbadion A **4a**, bisnorbadioquinone A **5a** and *O*-methylpulviquinone A **6b** are also obtained. The pigments can be easily recognized on TLC plates by their color reaction with ammonia vapor (Table 1).

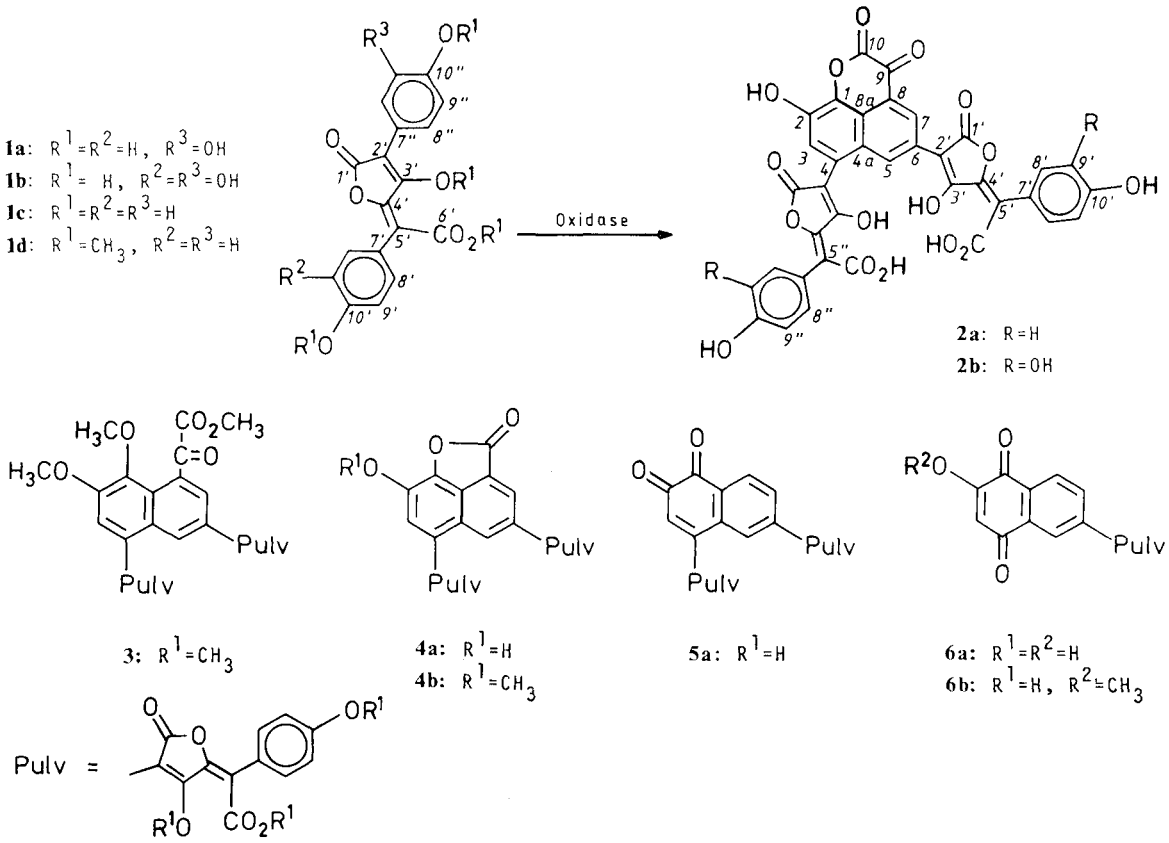

Table 1. Thin-layer chromatographic characterization of the cap cuticle pigments.

Pigment	R_F [a]	Color	Color over NH_3	Rel. amount [b]
2a	0.83 (I)	brown	green	100
4a	0.89 (I)	yellow-brown	salmon color	30
5a	0.83 (I)	brown	violet	10
6b	0.24 (II)	yellow-brown	red-violet	2

[a] I: TLC-Al foil aluminum oxide 150 F_{254} Merck, impregnated with saturated ethanolic ascorbic acid solution (eluent: 2-butanone/formic acid/water = 15:3:2); II: TLC-Al foil silica gel 60 F_{254} Merck (eluent: benzene/ethyl formate/formic acid = 10:5:3). [b] Referred to **2a** = 100.

Badion A **2a** forms blackish brown, shiny microcrystals, which decompose without defined melting point above 250°C and do not furnish any molecular ions with the usual MS techniques (EI, FD, FAB). According to elemental analyses and the X-ray emission spectra both **2a** as well as **4a** contain potassium, which can be removed only with difficulty, even by washing with dilute hydrochloric acid. The reddish brown solution of **2a** in methanol shows absorption maxima at $\lambda_{max} = 260$, 368, and 482 nm (sh). The ^{1}H-NMR spectrum ([D]$_6$DMSO) shows a singlet at $\delta = 7.31$ (1H) and two 1.5 Hz doublets at unusually low field ($\delta = 9.06$ and 9.26, 2H) besides the signals for two *p*-hydroxyphenyl moieties. Methylation with dimethyl sulfate/potassium carbonate in acetone affords a lemon-yellow nonamethyl derivative **3**, m.p. 255—257°C, which, according to high resolution MS, has the empirical formula $C_{45}H_{38}O_{17}$.

This indicates **2a** as having a C_{36} skeleton, and thus a biogenesis by oxidative dimerization of xerocomic acid **1a** ($C_{18}H_{12}O_7$). **1a** has already been isolated from the bay bo-letus[1] and recognized as a component responsible for the blue coloration of the flesh on being damaged[2]. Indeed, it is found on comparing the coupled ^{13}C-NMR spectra of **2a** and **3** with those of atromentic acid **1c** and its permethyl derivative **1d** that **2a** contains two pulvinic acid substructures (Table 2). Systematic selective decouplings, paying special attention to long-distance coupling, shows that the two pulvinic acid moieties in **3** are located at the 4,6-positions of a naphthalene nucleus bearing two methoxy groups in the 1,2-position and a CH_3O_2C—CO moiety at the 8-position.

Since the low-temperature ^{1}H-NMR spectrum ([D$_6$]acetone, 170 K) of **2a** shows only signals for three protons at $\delta = 9.51$, 9.63, and 10.70 in the region characteristic for phenolic OH groups, i.e. between $\delta = 9.5-11$, it must be present as naphtho[1,8-*bc*]pyrandione[4]. Hence, the methylation of **2a** to **3** proceeds via opening of the lactone ring. The structure **2a** fully explains the downfield position of the NMR signals of H-5 and H-7, since these protons are exposed to the deshielding effect of both the 9-carbonyl group as well as that of the pulvinic acid moiety on C-6[5].

Methylation of norbadion A **4a** furnishes a heptamethyl derivative $C_{42}H_{32}O_{15}$ **4b**, m.p. 247—249°C. The ^{1}H-NMR spectrum of **4a** is almost the same as that of **2a**[6], and, according to the ^{13}C-NMR data, it contains a dihydroxy-

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Table 2. ^{13}C-NMR data of **2a**, **3**, **1c**, and **1d** (100.62 MHz, δ-values, solvent as internal standard).

	2a ([D$_6$]DMSO]	**3** ($CDCl_3$)		**2a** ([D$_6$]DMSO)	**3** ($CDCl_3$)	**1c** (CD_3OD)	**1d** ($CDCl_3$)
C-1	130.60 d 7.1	142.41 dq 6.8/3.8	C-1′/1″	168.50 s	167.40 s	168.7 s	168.1 s
C-2	142.57 d 2.3	148.87 dq 2.1/3.8		168.51 s	168.00 s		
C-3	121.86 D 162	119.55 D 160	C-2′/2″	95.30 d 4.8	102.70 d 5	105.0 t 4.3	108.2 t 4.3
C-4	127.96 dd 5/1.5	123.80 dd 4.8/1.9		93.44 dd 4.3/4.0	106.20 t 4.8		
C-4a	125.67 dd 8.6/1.2	128.01 dd 8/1.2	C-3′/3″	166.72 s	163.65 q 3.8	160.8 s	162.2 s
C-5	131.16 Dd 165/6.5	129.66 Dd 162/6		166.92 s	164.45 q 3.8		
C-6	128.92* br. s	133.92 br. s	C-4′/4″	151.54 s	139.42 s	154.6 s	140.3 s
C-7	126.09 Dd 165/7.4	128.23 Dd 164/7.3		151.89 s	139.79 s		
C-8	125.29* br. s	125.01 br. s	C-5′/5″	117.89 t 3.9	117.09 t 4.2	118.3 t 4.0	115.6 t 4.2
C-8a	119.94 dd 6.8/7.3	126.74 dd 6.7/6.6		117.93 t 3.9	117.69 t 4.2		
C-9	173.03 d 4.5	187.30 d 4.8	C-6′/6″	171.38 s	166.87 q 3.8	174.8 s	167.4 q 4
C-10	154.75 s	161.19 q 3.8		172.23 s	166.96 q 3.8		
			C-7′/7″	126.16 t 8	123.29 t 8	125.6 t 8.2	123.6 t 8
				126.33 t 8	123.43 t 8	122.1 t 8.2	120.6 t 8
			C-8′/8″**	131.44 Dd 162/7.2	130.88 Dd 161/7.3	130.3 Dd 160/7.2	130.8 Dd 161/7
				131.46 Dd 162/7.2	130.93 Dd 161/7.3	132.7 Dd 150/7.2	131.0 Dd 161/7
			C-9′/9″**	114.02 Dd 159/4.8	114.32 Dd 161/5	115.6 Dd 160/4.6	114.0 Dd 160/5
				114.16 Dd 159/4.8	114.35 Dd 161/5	116.2 Dd 160/4.6	114.3 Dd 160/5
			C-10′/10″	156.47 tt 9/2.7	160.57 m	158.6 m	160.1 m
				156.59 tt 9/2.7	160.69 m	158.7 m	160.5 m

3: 1-OCH_3 (60.5, Q, J=146.4 Hz), 2-OCH_3 (56.7, 145.0), 10-OCH_3 (52.9, 148.1), 3′/3″-OCH_3 (60.8/61.8, 148.4/148.4), 6′/6″-OCH_3 (52.7/52.8, 147.6/147.6), 10′/10″-OCH_3 (55.32/55.33, 144.2/144.2); **1d**: 3′-OCH_3 (60.9, Q, J=147.7 Hz), 6′-OCH_3 (52.7, 147.7), 10′/10″-OCH_3 (55.3, 144.6)

[*] Assignment may be reversed. [**] Signals for double the number of C atoms.

naphthalene moiety with two pulvinic acid side chains. The side chain at the 8-position, however, is one carbon atom shorter than the other, and forms a γ-lactone with the 1-OH group (^{13}C-NMR: δ(9-CO)=167.12, d, J=3.5 Hz, in [D$_6$]DMSO).

Apparently, the component **2a** of the fungus is capable of further degradation; in bisnorbadioquinone A **5a**[6] the side chain at the 8-position is missing, and the hydroxy groups are oxidized.

Formation of pulviquinone A **6a** from **5a** by oxidative elimination of the pulvinic acid chain at the 4-position is conceivable. The brownish red pigment is isolated as the methyl ether **6b**, which is most likely formed during the extraction with acidified methanol. In order to demonstrate the role of xerocomic acid **1a** as a biogenetic precursor of badion A **2a**, a portion of the cap cuticle was removed from a bay boletus and the underlying white flesh treated with aqueous xerocomic acid solution. The resulting yellow spot became bluish green within a few minutes and gradually turned brown in color. After extraction and chromatographic separation of the resulting pigment, **2a** could be detected ^{1}H-NMR spectroscopically. Thus, the enzymes necessary for the oxidative dimerization of **1a** appear to be fixed to the cap cuticle. Badion A **2a** is also the pigment of *Boletus pinicola* Vitt., a close relative of the cep. Interestingly, in *Boletus erythropus* (Fr. ex Fr.) Pers. it is replaced by badion B **2b**, which is biogenetically derived from variegatic acid **1b**[7].

Received: February 9, 1984 [Z 704 IE]
German version: *Angew. Chem. 96* (1984) 435

CAS-Registry numbers:
1c, 90320-59-5; **1d**, 90295-65-1; **2a**, 90295-66-2; **3**, 90295-67-3; **4a**, 90295-68-4; **4b**, 90295-69-5; **5a**, 90295-70-8; **6b**, 90295-71-9.

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[6] UV (MeOH). **4a**: λ_{max}=260, 367, 406 nm (sh); **4a**: 250 (sh), 307, 356, 415 nm (sh); **6a**: 265 (sh), 278, 312, 354, 422 nm.—^{1}H-NMR ([D$_6$]DMSO). **4a**: δ=6.76, 6.79, 7.09, 7.12 (each d, J=8.9 Hz, 8H), 7.39 (s, 1H), 9.04, 9.44 (each d, J=0.9 Hz, 2H); **5a**: 6.45 (s, 1H), 6.73, 6.75, 7.05, 7.08 (each d, J=8.5 Hz, 8H), 7.89 (d, J=8.2 Hz, 1H), 8.33 (dd, J=8.2 and 1.5 Hz, 1H), 8.53 (d, J=1.5 Hz, 1H), 9.46, 9.50, 17.56, 17.83 (each br. s, 4OH); **6b**: 3.83 (s, 3H), 6.28 (s, 1H), 6.73, 7.07 (each d, J=8.5 Hz, 4H), 7.93 (d, J=8.3 Hz, 1H), 8.56 (dd, J=8.3 and 1.6 Hz, 1H), 8.82 (d, J=1.6 Hz, 1H).
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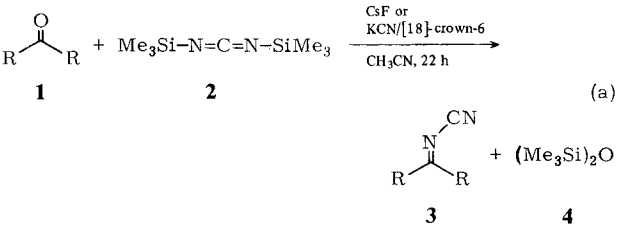
One-Step Entry to *N*-Cyanimines and to *N,N′*-Dicyanoquinonediimines, a Novel Class of Electron-Acceptors**

By *Alexander Aumüller* and *Siegfried Hünig**

N-Cyanimines **3** are accessible from alkenes and cyanazide[1], as well as from certain carbodiimides and isothiocyanates[2]. Hitherto all reactions in which ketones have been used as starting substances have involved several steps[3]. Herein we describe the one-step conversion $>C=O \rightarrow >C=N-CN$, which can be applied to (non-enolizing) ketones and to *p*-quinones. The crucial reagent is bis(trimethylsilyl)carbodiimide **2**[4], which converts, e.g., benzophenone (62—70%)[5] and fluorenone (75%)[5] into **3** in the presence of fluoride or cyanide catalysts according to equation (a).



1 **2** (a) **3** **4**

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[**] This work was supported by the Stiftung Volkswagenwerk, by the Fonds der Chemischen Industrie, and by BASF AG.