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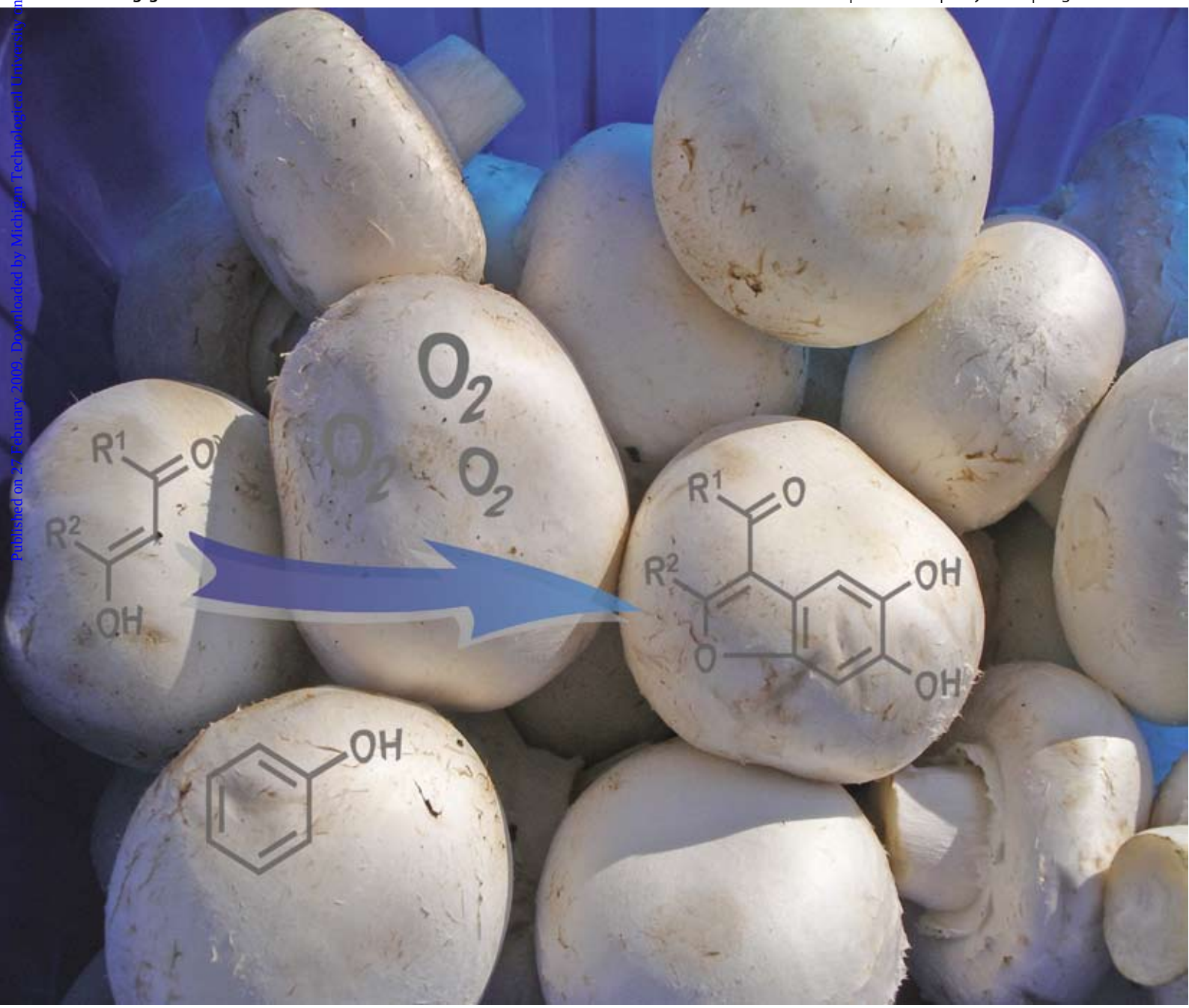

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Combined action of enzymes: the first domino reaction catalyzed by *Agaricus bisporus*

Heiko Leutbecher, Szilvia Hajdok, Christina Braunberger, Melanie Neumann, Sabine Mika, Jürgen Conrad and Uwe Beifuss*

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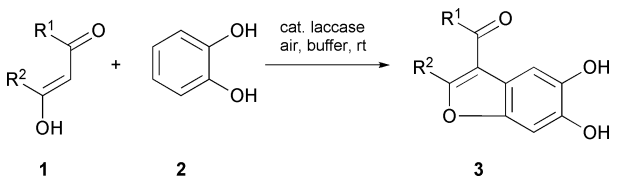
The enzymes tyrosinase and laccase from a crude extract of the button mushroom (*Agaricus bisporus*) can be employed to catalyze the domino reaction between phenol and various cyclic 1,3-dicarbonyls using atmospheric oxygen as the oxidizing agent and yielding annulated benzofuranes in a highly efficient and sustainable manner.

Enzyme-catalyzed reactions are gaining more and more importance in organic synthesis since they may often be conducted in a highly efficient and environmentally friendly fashion in aqueous solutions at room temperature.[1] In the chemical industry they are not only used in the synthesis of fine chemicals, but can also be applied for the production of bulk chemicals.[2]

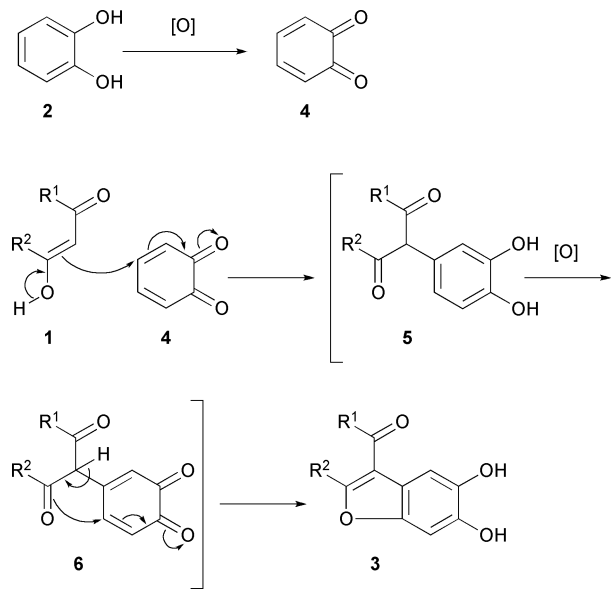
While a multitude of enzyme-catalyzed single-step transformations is known, relatively few domino reactions initiated by enzymes have been described,[3,4] and there are even fewer examples of the combined use of several enzymes in domino processes.[5]

Recently we have been able to transform the cyclic 1,3-dicarbonyls **1** with various catechols **2** into coumestanes and related *O*-heterocycles **3** using a laccase-catalyzed reaction with atmospheric oxygen as the oxidizing agent (Scheme 1).[6] The main characteristics of these reactions are that they can be easily performed under mild reaction conditions, that they use an ecologically benign and infinitely available oxidizing agent, and that their products can be separated and purified in a very simple way. Due to their phytoestrogenic, antibacterial, antifungal and antihepatotoxic effects, such heterocycles have an interesting biological profile.[7]



Scheme 1

It is assumed that the first step of the domino process is the laccase-catalyzed oxidation of the catechol **2** with O_2 to *o*-benzoquinone **4**, which then undergoes an *inter*molecular 1,4-addition with the enol of the 1,3-dicarbonyl **1** as a nucleophile to yield **5** (not isolable). A second laccase-catalyzed oxidation occurs (**5** → **6**) followed by a second 1,4-addition proceeding *intra*molecularly and forming the heterocycle **3**. Altogether, a domino oxidation/1,4-addition/oxidation/1,4-addition process has taken place (Scheme 2).



Scheme 2 Proposed mechanism of the domino reaction.

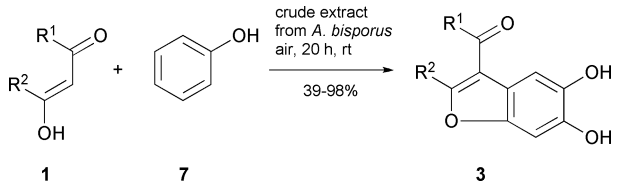
Unfortunately, phenols that are more easily accessible than the corresponding catechols cannot be used as the starting material for this reaction since laccases are unable to catalyze the phenol to catechol oxidation.[8] In order to directly employ phenols they would first have to undergo oxidation to the catechols. Since this reaction was supposed to be run in the presence of laccase in the same reaction flask using atmospheric oxygen as the oxidant, we restricted our search to suitable oxidizing enzymes. Amongst others, we came across tyrosinases, which are known for their ability to catalyze the O_2 oxidation of phenols to catechols.[9]

And there was another reason for combining the tyrosinase with a laccase: both enzymes co-occur in various fungi, including the cultivated and thus easily and abundantly accessible button mushroom (*Agaricus bisporus*) making it a very inexpensive source of both enzymes.[10] The fact that *A. bisporus* contains tyrosinase and laccase, among other enzymes, has long been known but—apart from a few studies on the oxidative degradation of phenolic compounds in industrial effluents[11]—rarely been exploited. As far as we know no defined chemical

Bioorganische Chemie, Institut für Chemie, Universität Hohenheim, Garbenstr. 30, D-70599, Stuttgart, Germany.
E-mail: ubeifuss@uni-hohenheim.de; Fax: (+49) 711 459 22951; Tel: (+ 49) 711 459 22171

transformation, let alone a domino reaction, has been reported using a crude extract from *A. bisporus* as the catalyst. However, there have been numerous reports on various reactions with either pure tyrosinases[9,12] or pure laccases.[13] There are also several examples of tyrosinase or laccase catalyzed oxidations followed by chemical transformations.[6,14]

Here, we report the first example of the combined action of a tyrosinase and a laccase for a domino process. We have found that the efficient and sustainable reaction between the phenol (**7**) and the cyclic 1,3-dicarbonyls **1a–g** using a crude extract from the fruiting bodies of *A. bisporus* as the catalyst and atmospheric oxygen as the oxidant resulted in the selective formation of coumestanes and related *O*-heterocycles (**3a–g**) (Scheme 3).



1 **7** **3**

Scheme 3

First, we developed a very simple procedure for the preperation of a crude extract from *A. bisporus*. The fruiting bodies were homogenized with 0.2 M phosphate buffer (pH = 6.0) and filtered at 4 °C.† The supernatant obtained after centrifugation was used directly and without further purification to perform the transformations: the 1,3-dicarbonyls **1a–g** were stirred with a small excess of the phenol (**7**) under air at room temperature for 20 h (Scheme 3, Table 1).‡

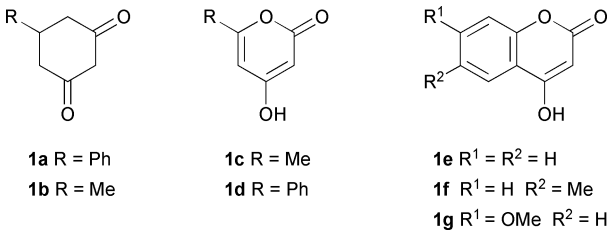
We assume that the monooxygenase tyrosinase initially catalyzes the oxidation of the phenol (**7**) to achieve the catechol (**2**), which can be detected by thin-layer chromatography during the reaction. Tyrosinase- and/or laccase-catalyzed oxidation of **2** follows to give the *o*-quinone (**4**), which then reacts with **1a–g** to produce the *O*-heterocycles **3a–g**. Presumably, the domino reaction between **4** and **1a–g** follows the mechanism described above (Scheme 2).

Different 1,3-dicarbonyls **1** (Fig. 1) were reacted with **7**. Reactions were accomplished with the cyclic 1,3-diketones **1a** and **1b** (Table 1, entry 1 and 2), the 6-substituted 4-hydroxy-2*H*-pyran-2-ones **1c** and **1d** (Table 1, entry 3 and 4) as well as the substituted 4-hydroxy-2*H*-chromen-2-ones **1e–g** (Table 1, entries 5–7). The heterocycles **3a–g** (Fig. 2) were obtained as the sole reaction products with yields ranging from 39 to 98%.§ The

Table 1 Reaction of **7** with **1a–g** to yield **3a–g**

Entry	**7** (equiv.)	1,3-Dicarbonyl **1**	**3**	Yield (%)
1	1.2[a]	**a**	**a**	44[b]
2	1.3	**b**	**b**	39
3	1.3	**c**	**c**	48
4	2.2[a]	**d**	**d**	66[c]
5	1.1	**e**	**e**	88
6	1.2	**f**	**f**	98
7	1.3	**g**	**g**	72[b]

[a] The reaction was run in a buffer/acetone mixture (v/v = 10:1). [b] Yield after recrystallization of the crude product. [c] **3d** was transformed into the corresponding bisacetate with 71% yield.



1a R = Ph
1b R = Me
1c R = Me
1d R = Ph
1e $R^1 = R^2 = H$
1f $R^1 = H$ $R^2 = Me$
1g $R^1 = OMe$ $R^2 = H$

Fig. 1 1,3-Dicarbonyls **1a–g** for the domino reaction with **7**.

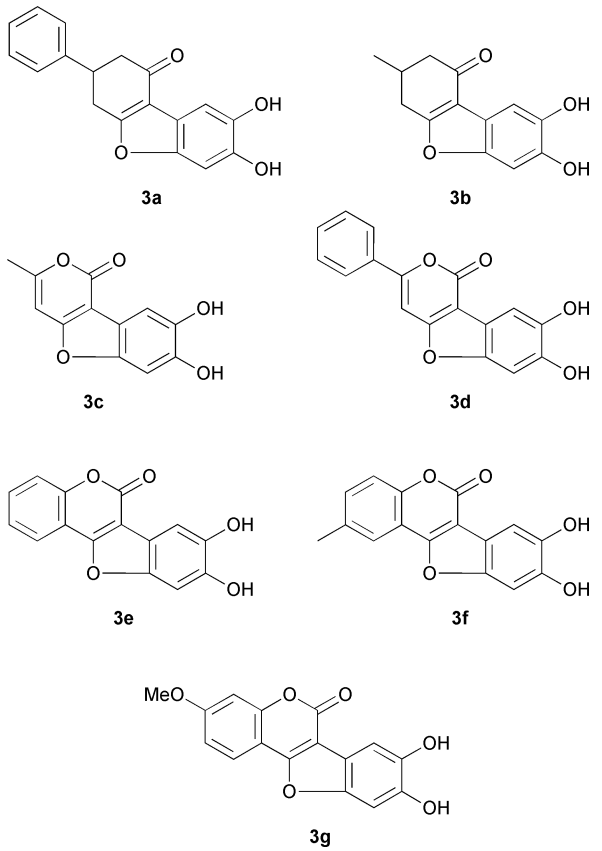


Fig. 2 Products **3a–g** of the domino reaction between **1a–g** with **7**.

highest yields were observed with the reactions involving **1e–g**. The 8,9-dihydroxy-6*H*-benzofuro[3,2-*c*]chromen-6-one **3e**, for example, was obtained with 88%, **3f** with 98% and **3g** with 72% yield. The work-up of the reaction mixture was as easy as the reaction process itself, since the crude products could be obtained from the reaction mixture by a simple salting-out procedure.

Following the extraction of the crude products with a suitable solvent (ethanol or acetone), filtration and removal of the solvent *in vacuo*, compounds with a purity of 90–95% were obtained (^{1}H NMR). Only three of them needed to be further purified through recrystallization (**3a** and **3g**) or transformation into the bisacetate (**3d**). Using non-polar solvents for the extraction step led to lower yields, while more polar solvents led to less pure products. All 1,3-dicarbonyls could be reacted with 1.1 to 1.3 equiv. of **7**, except **1d**. In the latter case 2.2 equiv. of **7** were required to achieve a complete transformation (Table 1, entry 4).

In order to elucidate the role that both enzymes play in this domino reaction, several additional experiments were conducted. In one experiment we tried to react **7** and **1e** under standard reaction conditions (0.5 mmol **1e**, 0.55 mmol **7**, 45 mL 0.2 M phosphate buffer pH = 6.0, 20 h at room temperature) using a commercial preparation of laccase from *A. bisporus* (Fluka): not even a trace of the heterocycle **3e** could be detected, and **1e** was quantitatively recovered after 20 h. Under the standard conditions specified above, **7** was completely transformed into products that could not be identified; they are supposed to be oligomeric and polymeric products of oxidative phenol coupling. From earlier studies we knew that the oxidative reaction of catechol (**2**) with **1e** forming **3e** is catalyzed by laccase.[6] Consequently, the laccase is not able to catalyze the oxidation of phenol (**7**) to catechol (**2**). In another control experiment, **7** and **1e** were reacted with 7425 U of a commercially available tyrosinase from cultivated mushroom (Sigma) under standard reaction conditions. Although the product **3e** could be isolated after 20 h, the 49% yield was considerably lower than that obtained from the reaction with the crude extract from *A. bisporus* (88%; Table 1, entry 5). This is even more astonishing since the activity of the commercial preparation of tyrosinase was higher by a factor of 1.5 than that of the tyrosinase in the crude fungal extracts (4815 U).¶ The experiment demonstrates the superiority of the laccase/tyrosinase combination over tyrosinase alone, which might be due to the fact that the laccase co-operates in the oxidation of the catechol (**2**) forming the *o*-quinone (**4**). This interpretation is supported by the result of the reaction between **1e** and **7**, where 41.7 U of pure laccase (from *Agaricus bisporus*, Fluka)‖ was added to pure tyrosinase (from mushroom, Sigma) of the same activity as in the second control experiment (7425 U). Under these conditions **3e** was isolated with 69% yield after 20 h. If **1e** and **7** were reacted with 4815 U tyrosinase (activity of the mushroom extract) and 110 U pure laccase, side reactions are observed, and the yield of **3e** drops to 59%.

In summary, a crude extract from *A. bisporus*, which can be produced by a most simple procedure, was demonstrated to catalyze the efficient and sustainable synthesis of annulated benzofuranes **3** under mild reaction conditions by reacting phenol (**7**) with the 1,3-dicarbonyls **1** using oxygen as an oxidant.

Acknowledgements

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Notes and references

† Preparation of the mushroom extract: fresh commercial mushrooms (64 g) were homogenized in ice-cold 0.2 M phosphate buffer pH 6.0 (500 mL). After filtering, the homogenate was centrifuged (4185 × *g* for 5 min). The collected supernatants were directly used as medium for the reaction of **7** with **1a–g**. The mushroom extract can be stored at –20 °C.

‡ General procedure for synthesis of **3a–g**: 1.0 equiv. **1** (0.5 mmol) [**1a** (0.3 mmol), **1d** (0.2 mmol) respectively] and 1.1 to 2.2 equivs. **7** (see Table 1) were dissolved in 45 mL of mushroom extract. For **1a** and **1d** 4.5 mL of acetone were added. The reaction mixture was stirred vigorously at room temperature for 20 h while complete consumption of the substrates occurred. The mixture was saturated with sodium chloride and filtered through a buchner funnel. The filter cake was washed with 15% sodium chloride solution (75 mL) and water (20 mL) and dried at room temperature. The fine powdered crude product was extracted with 150 mL of boiling acetone (**3a–d**) or ethanol (**3e–g**), respectively. After filtration the solvent was evaporated *in vacuo* to yield nearly pure heterocycles **3a–g**. **3a** was recrystallized from acetone and **3g** from a mixture of ethanol/H_2O. **3d** (108 mg, 0.37 mmol) was dissolved in 2 mL (1.96 g, 24.7 mmol) of pyridine, treated with 250 µL (270 mg, 2.6 mmol) acetic anhydride and 7 mg (0.06 mmol, 15 mol%) of DMAP. The reaction mixture was stirred for 2.5 h and 14 mL of 2 M HCl were added. The precipitate (99 mg of **8d**, 71%) was collected by filtration, washed with saturated sodium bicarbonate solution and water, dried and recrystallized from ethanol.

§ Selected analytical data for 3,4-dihydro-7,8-dihydroxy-3-phenyl-dibenzofuran-1(2*H*)-one (**3a**): $\lambda_{max}(CH_3CN)$/nm 299 (lg ε 3.94), 238 (4.28) and 207 (4.61); ν_{max}(atr)/cm^{-1} 3433 and 3107 (OH), 1630 (C=O), 1615, 1580 and 1518 (C=C), 1437 (CH_2), 1286 (OH), 1270 and 1040 (C–O), 869, 771 and 698 (=C–H); δ_H(300 MHz; DMSO-d_6) 2.58 (dd, $^2J_{2\text{-HA},2\text{-HB}} = 16.2$ Hz, $^3J_{2\text{-HA},3\text{-H}} = 3.9$ Hz, 1H, 2-H_A), 2.94 (dd, $^2J_{2\text{-HB},2\text{-HA}} = 16.2$ Hz, $^3J_{2\text{-HB},3\text{-H}} = 12.3$ Hz, 1H, 2-H_B), 3.16–3.30 (m, 2H, 4-H_2), 3.60–3.74 (m, 1H, 3-H), 7.01 (s, 1H, 6-H or 9-H), 7.26 (s, 1H, 6-H or 9-H), 7.27 (t, $^3J_{4'\text{-H},3'\text{-H}} = {}^3J_{4'\text{-H},5'\text{-H}} = 7.5$ Hz, 1H, 4′-H), 7.36 (t, $^3J_{3'\text{-H},2'\text{-H}} = {}^3J_{3'\text{-H},4'\text{-H}} = {}^3J_{5'\text{-H},4'\text{-H}} = {}^3J_{5'\text{-H},6'\text{-H}} = 7.3$ Hz, 2H, 3′-H and 5′-H), 7.43 (d, $^3J_{2'\text{-H},3'\text{-H}} = {}^3J_{6'\text{-H},5'\text{-H}} = 7.2$ Hz, 2H, 2′-H and 6′-H), 9.14 (s, 1H, OH), 9.17 (s, 1H, OH); δ_C(75 MHz; DMSO-d_6) 31.36 (C-4), 41.03 (C-3), 45.33 (C-2), 99.23, 106.11 (C-6 or C-9), 114.96 (C-9a), 116.22 (C-9b), 127.55 (C-4′), 127.79 (C-2′and C-6′), 129.27 (C-3′ and C-5′), 143.79 (C-1′), 144.53, 145.21, 149.02 (C-5a, C-7 or C-8), 169.66 (C-4a), 193.74 (C-1); *m*/*z*(EI, 70 eV) 294.0903 (M$^+$, 100%. $C_{18}H_{14}O_4$ requires 294.0892), 252 (10), 190 (98), 162 (53), 134 (5), 92 (5), 69 (4). Selected analytical data for 3,4-dihydro-7,8-dihydroxy-3-methyl-dibenzofuran-1(2*H*)-one (**3b**): (found: C, 66.97; H, 5.02. $C_{13}H_{12}O_4$ requires C, 67.23; H, 5.21%); $\lambda_{max}(CH_3CN)$/nm 299 (lg ε 3.91), 237 (4.22) and 207 (4.47); ν_{max}(atr)/cm^{-1} 3470 and 3119 (OH), 1628 (C=O), 1578 and 1518 (C=C), 1293 (OH), 1247 and 1040 (C–O), 876 and 810 (=C-H); δ_H(300 MHz; DMSO-d_6) 1.13 (d, $^3J_{3\text{-CH3},3\text{-H}} = 6.3$ Hz, 3H, 3-CH_3), 2.32 (dd, $^2J_{2\text{-HA},2\text{-HB}} = 16.5$ Hz, $^3J_{2\text{-HA},3\text{-H}} = 12.0$ Hz, 1H, 2-H_A), 2.43 (m, 1H, 3-H), 2.45 (dd, $^2J_{2\text{-HB},2\text{-HA}} = 16.2$ Hz, $^3J_{2\text{-HB},3\text{-H}} = 3.0$ Hz, 1H, 2-H_B), 2.71 (dd, $^2J_{4\text{-HA},4\text{-HB}} = 17.4$ Hz, $^3J_{4\text{-HA},3\text{-H}} = 9.3$ Hz, 1H, 4-H_A), 3.04 (dd, $^2J_{4\text{-HB},4\text{-HA}} = 17.5$ Hz, $^3J_{4\text{-HB},3\text{-H}} = 4.7$ Hz, 1H, 4-H_B), 6.98 (s, 1H, 6-H or 9-H), 7.22 (s, 1H, 6-H or 9-H), 9.09 (s, 1H, OH), 9.13 (s, 1H, OH); δ_C(75 MHz; DMSO-d_6) 21.37 (3-CH_3), 30.97 (C-3), 31.65 (C-4), 46.34 (C-2), 99.17, 106.07 (C-6 or C-9), 115.03 (C-9a), 115.98 (C-9b), 144.41, 145.06, 148.88 (C-5a, C-7 or C-8), 170.02 (C-4a), 194.63 (C-1); *m*/*z*(EI, 70 eV) 232 (M$^+$, 100%), 217 (M$^+$ – CH_3, 2), 190 (52), 162 (49), 134 (4), 92 (4), 69 (4).

¶ Tyrosinase activity was determined following a modified procedure taken from ref. 10: a 1 mM solution of tyrosine (2 mL) in 0.1 M phosphate buffer (pH = 6.0) was mixed with (a) a solution of commercially available tyrosinase (from mushroom, Sigma) in phosphate buffer (1 mL) or (b) with crude mushroom extract (1 mL). The change in absorption was followed *via* UV-spectroscopy (λ = 310 nm). One unit was defined as a change in absorption of 0.001 at pH = 6.0 at room temperature. The activity of the crude mushroom extract amounted to 107 U mL^{-1}. The activity of commercial tyrosinase amounted to 165 U mL^{-1} in a total volume of 45 mL reaction mixture.

‖ Laccase activity was determined following a modified procedure taken from E. J. Land, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 803–810 and M. Felici, F. Artemi, M. Luna, M. Speranza, *J. Chromatogr., A*, 1985, **320**, 435–439. A 1.18 M solution of catechol (0.3 mL) in 0.2 M phosphate buffer (pH = 6.0) was diluted with 0.2 M phosphate buffer (2.5 mL, pH = 6.0) and treated with a solution of laccase in the same buffer (0.2 mL). The change in absorption was followed *via* UV-spectroscopy (λ = 390 nm). One unit was defined as the amount of laccase that converts 1 µmol of catechol per minute at pH = 6.0 at room temperature. The activity of laccase amounted to 0.926 U mL^{-1} in the reaction mixture for the reaction of **1e** with **7** (total volume of 45 mL). The laccase activity in the mushroom extract cannot be determined with the laccase-specific syringaldazine,[10] since the laccase activity is below the detection limits of this assay. However, the total activity (tyrosinase and laccase) of the extract concerning the oxidation of catechol significantly exceeds that of the tyrosinase activity of the mushroom extract; the latter can be estimated by determining the activity of pure tyrosinase with both catechol and tyrosine and by using these values to derive the tyrosinase activity of the mushroom extract, which was determined through the reaction with tyrosin, from the tyrosinase

activity towards the other substrate. The activity of the laccase added in the third control experiment is below the detection limit of the syringaldazine assay, too.

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