Synlett U. Kober, H.-J. Knölker Letter

Palladium-Catalyzed Approach to Malasseziazole A and First Total Synthesis of Malasseziazole C

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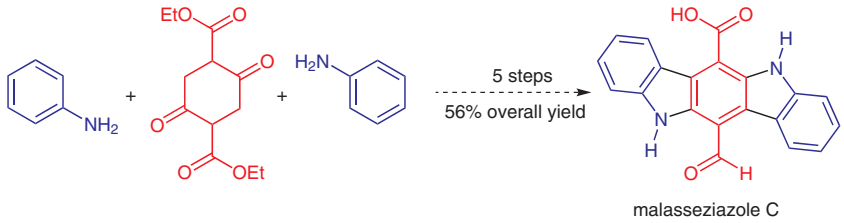
Dedicated to Professor K. Peter C. Vollhardt on the occasion of his 69th birthday



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Abstract We describe a convergent route to 5,11-dihydroindolo[3,2-*b*]carbazoles using a twofold oxidative cyclization as key step. The method has been applied to the synthesis of a precursor for malasseziazole A and to the first total synthesis of malasseziazole C.

Key words alkaloids, catalysis, cyclization, indolocarbazoles, natural products, palladium

The human lipophilic yeast *Malassezia furfur* is believed to be one of the fungi which in their pathogenic mycelial form cause the common skin disease pityriasis versicolor, a fungal infection leading to mild inflammation of the skin and characteristic colored lesions.[1] Steglich et al. described the isolation and structural elucidation of eleven new alkaloids from cultures of *Malassezia furfur*, among them the malasseziazoles A–C (**1**–**3**) and pityriazole (**4**, Figure 1).[2] These compounds were shown to be tryptophan metabolites generated via indol-3-ylpyruvate and some of them may be involved in the pathogenesis of pityriasis versicolor.[3] The structural variety and the broad range of biological activities of carbazole alkaloids have been extensively investigated.[4,5] Also the chemistry of indolocarbazoles has been studied in detail.[5,6] However, till 2002 all indolocarbazole alkaloids isolated from nature were limited to indolo[2,3-*a*]carbazole derivatives.[5,6b,c] Thus, the compounds **1**–**4** found by Steglich et al. are structurally unique, as the malasseziazoles A–C (**1**–**3**) represent the first 5,11-dihydroindolo[3,2-*b*]carbazole alkaloids and pityriazole (**4**) is the first 1-(indol-3-yl)carbazole isolated from natural sources.

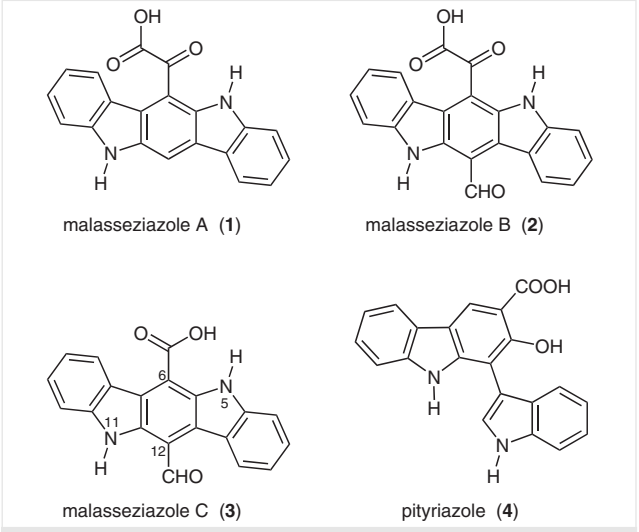
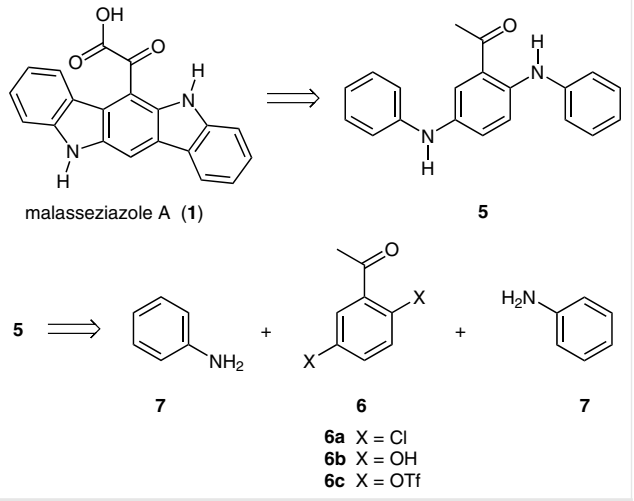


Figure 1 Malasseziazoles A–C (**1**–**3**) and pityriazole (**4**)

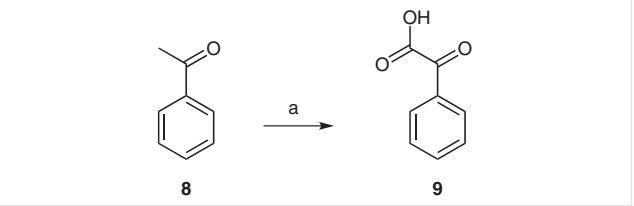
Bergman et al. have developed synthetic routes to 5,11-dihydroindolo[3,2-*b*]carbazoles.[6a,c,7–9] 5,11-Dihydroindolo[3,2-*b*]carbazole-6-carbaldehyde and 5,11-dihydroindolo[3,2-*b*]carbazole-6,12-dicarbaldehyde are formed by photolysis of a tryptophan solution and represent strongly binding ligands for the aryl hydrocarbon receptor.[10] Bergman's group reported efficient syntheses of both compounds.[7,8]

Previously, we have already reported the first total synthesis of pityriazole (**4**).[11] In the present paper,[12] we describe an approach to a potential precursor for the synthesis of malasseziazole A (**1**) and the first total synthesis of malasseziazole C (12-formyl-5,11-dihydroindolo[3,2-*b*]carbazole-6-carboxylic acid) (**3**).



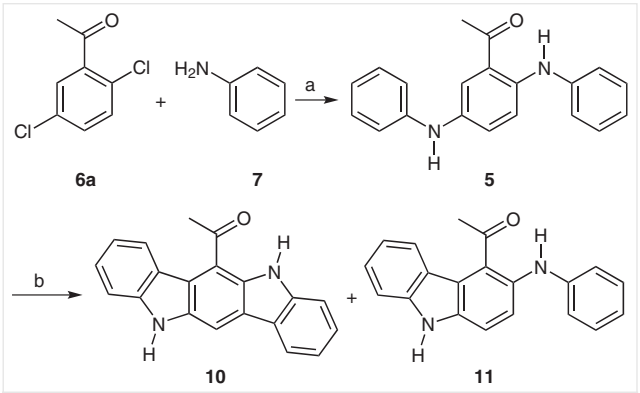
Scheme 1 Retrosynthetic analysis of malasseziazole A (**1**)

The synthetic plan for malasseziazole A (**1**) is based on our well-established palladium-catalyzed synthesis of carbazoles.[13,14] Key feature of our approach is a bidirectional indole annulation, which was applied earlier to the synthesis of indolo[2,3-*b*]carbazole from *m*-phenylenediamine via our iron-mediated synthesis.[15] Thus, malasseziazole A (**1**) should be formed by twofold palladium(II)-catalyzed oxidative cyclization of 2′,5′-bis(phenylamino)acetophenone (**5**) followed by oxidation of the acetyl side chain to an α-keto acid (Scheme 1). Compound **5** could derive from double Buchwald–Hartwig coupling of the 2′,5′-disubstituted acetophenone **6** with aniline (**7**). In a model study, we achieved the oxidation of acetophenone (**8**) to the corresponding α-keto acid **9** in high yield following the procedure reported by Zhang et al. (Scheme 2).[16]



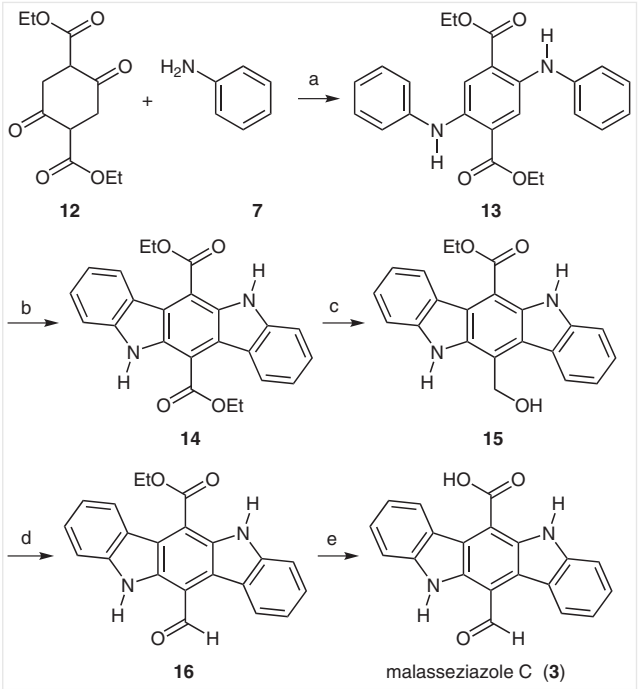
Scheme 2 Oxidation of acetophenone (**8**) to 2-oxo-2-phenylacetic acid (**9**). *Reagents and conditions*: (a) SeO_2 (2 equiv), pyridine, 120 °C, 18 h, 83%.

The palladium(0)-catalyzed Buchwald–Hartwig coupling of 2′,5′-dichloroacetophenone (**6a**) with 2.1 equivalents of aniline in the presence of catalytic amounts of SPhos[17] as ligand led to 2′,5′-bis(phenylamino)acetophenone (**5**)[18] in high yield (Scheme 3). The Buchwald–Hartwig amination of the 2′,5′-bistriflate **6c**, which is readily prepared from the corresponding 2′,5′-dihydroxy compound **6b** (3 equiv Tf_2O, 6 equiv 2,6-lutidine, CH_2Cl_2, –15 °C to r.t., 16 h, 81% **6c**), provided compound **5** in only moderate yield. The oxidative cyclization of **5** under the conditions previously applied[11,19] led to the 6-acetyl-5,11-dihydroindolo[3,2-*b*]carbazole (**10**, 12% yield)[20] along with the monocyclized product **11** (23% yield)[21] and starting material. The fact that only one regioisomeric monocyclized product was formed as byproduct has been ascribed to an acetyl-directed palladation generating an acetyl-coordinated palladium(II) complex.[22] Subsequent reductive elimination leads to the 4-acetyl-substituted carbazole derivative **11**, which on further cyclization provides compound **10**. An optimization of this oxidative cyclization is still being explored.



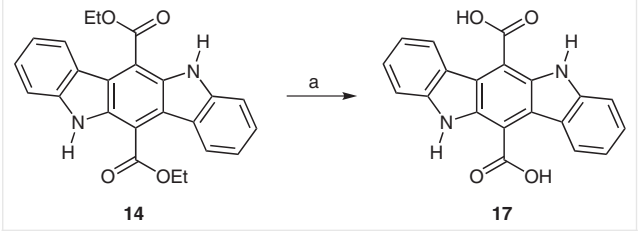
Scheme 3 Synthesis of the 5,11-dihydroindolo[3,2-*b*]carbazole **10**. *Reagents and conditions*: (a) aniline (**7**, 2.1 equiv), $Pd(OAc)_2$ (10 mol%), SPhos (20 mol%), Cs_2CO_3 (2.1 equiv), toluene, reflux, 2 d, 77%; (b) $Pd(OAc)_2$ (30 mol%), K_2CO_3 (30 mol%), PivOH, 85 °C, air, 19 h, 12% **10**, 23% **11**, 21% **5**.

For the first total synthesis of malasseziazole C (**3**), we decided to follow the route described by Bergman et al. for the synthesis of 6,12-disubstituted indolo[3,2-*b*]carbazoles.[8] Condensation of diethyl cyclohexane-1,4-dione-2,5-dicarboxylate (**12**) with an excess of aniline (**7**) afforded diethyl 2,5-bis(phenylamino)terephthalate (**13**) as reported by Liebermann more than a century ago (Scheme 4).[23] Our original conditions for the palladium(II)-catalyzed oxidative cyclization [30 mol% $Pd(OAc)_2$, 5 equiv $Cu(OAc)_2$, AcOH, microwave, 130 °C, 3 h],[24] provided the desired diethyl 5,11-dihydroindolo[3,2-*b*]carbazole-6,12-dicarboxylate (**14**) in only 38% yield along with 28% of the monocyclized product and 27% of starting material. The conditions first described by Åkermark et al. for the cyclization of electron-deficient diarylamines (two equivalents of palladium(II) acetate in acetic acid at 100 °C),[25,26] afforded compound **14** in 69% yield. The selective reduction of **14** described by Bergman et al.[8] led to the monoalcohol **15** in 92% yield. Oxidation of the monoalcohol **15** using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) afforded the monoaldehyde **16**.[8,27] Finally, ester cleavage of **16** provided quantitatively malasseziazole C (**3**),[28] which is identical to the natural product according to its spectroscopic data.[2]



Scheme 4 Synthesis of malasseziazole C (**3**). *Reagents and conditions*: (a) aniline (**7**, 2.4 equiv), AcOH, 100 °C, air, 12 h, 96%; (b) $Pd(OAc)_2$ (2.2 equiv), AcOH, 100 °C, 3 h, 69%; (c) $LiAlH_4$ (2.0 equiv), THF, 0 °C, 30 min, 92%; (d) DDQ (1.3 equiv), 1,4-dioxane, r.t., 2 h, 92%; (e) KOH (100 equiv), EtOH–H_2O (1:1), reflux, 30 min, 100%.

Saponification of compound **14** afforded 5,11-dihydroindolo[3,2-*b*]carbazole-6,12-dicarboxylic acid (**17**) in high yield (Scheme 5).[29] The diacid **17** should have a better solubility in water, which would be advantageous for projected bioactivity studies. Moreover, as a potential oxidation product of malasseziazole C (**3**), compound **17** could also be a natural product.



Scheme 5 Synthesis of 5,11-dihydroindolo[3,2-*b*]carbazole-6,12-dicarboxylic acid (**17**). *Reagents and conditions*: (a) KOH (100 equiv), EtOH–H_2O (1:1), reflux, 1 h, 86%.

In conclusion, using a bidirectional indole annulation as the key step, we have achieved an approach to the 5,11-dihydroindolo[3,2-*b*]carbazole alkaloid malasseziazole A (**1**). Moreover, we have completed the first total synthesis of malasseziazole C (**3**) thus confirming the structural assignment for this natural product. Via the present route, malasseziazole C (**3**) is available in five steps and 56% overall yield based on cheap commercial starting materials.

Acknowledgment

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1380713.

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(18) **2′,5′-Bis(phenylamino)acetophenone (5)**
Orange oil. IR (ATR): ν = 3380, 3276, 3034, 2921, 2851, 1641, 1619, 1595, 1575, 1512, 1492, 1465, 1420, 1398, 1360, 1306, 1245, 1204, 1076, 1025, 994, 957, 933, 874, 814, 743, 692, 664 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 2.57 (s, 3 H), 6.74 (t, *J* = 7.3 Hz, 1 H), 6.94–7.03 (m, 3 H), 7.17–7.20 (m, 4 H), 7.25–7.33 (m, 4 H), 7.62 (d, *J* = 1.9 Hz, 1 H), 7.98 (br s, 1 H), 9.88 (br s, 1 H). ^{13}C NMR and DEPT (125 MHz, DMSO-d_6): δ = 28.53 (CH_3), 114.91 (2 CH), 116.81 (CH), 118.57 (CH), 120.01 (2 CH), 121.68 (C), 122.00 (CH), 122.10 (CH), 126.81 (CH), 129.26 (2 CH), 129.49 (2 CH), 133.98 (C), 139.91 (C), 141.46 (C), 144.89 (C), 201.24 (C=O). MS (EI): *m/z* = 302 (100), 287 (12), 285 (10), 256 (10), 195 (47), 183 (16), 167 (54), 166 (22), 154 (14), 128 (13), 77 (18), 51 (9). Anal. Calcd (%) for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.26. Found: C, 79.42; H, 5.99; N, 9.16.

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(20) **6-Acetyl-5,11-dihydro-indolo[3,2-*b*]carbazole (10)**
Yellow solid; mp 244 °C. UV (MeOH): λ = 213 (sh), 223, 254, 306, 338 (sh), 357, 438 nm. Fluorescence (MeOH): λ_{ex} = 223 nm, λ_{em} = 507 nm. IR (ATR): ν = 3456, 3400, 3051, 2920, 2851, 1640, 1605, 1558, 1512, 1457, 1418, 1353, 1320, 1292, 1270, 1221, 1186, 1168, 1144, 1109, 1010, 988, 961, 934, 866, 739, 692, 641, 621 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ = 2.96 (s, 3 H), 7.23–7.28 (m, 2 H), 7.46–7.49 (m, 3 H), 7.51–7.52 (m, 1 H), 8.10 (d, *J* = 7.8 Hz, 1 H), 8.17 (d, *J* = 8.1 Hz, 1 H), 8.22 (s, 1 H), 8.28 (br s, 1 H), 9.72 (br s, 1 H). ^{13}C NMR and DEPT (150 MHz, $CDCl_3$): δ = 30.93 (CH_3), 106.42 (CH), 110.95 (CH), 111.00 (CH), 115.07 (C), 119.26 (CH), 119.46 (CH), 120.26 (C), 120.31 (CH), 121.90 (C), 122.37 (C), 124.08 (CH), 124.25 (C), 126.40 (CH), 126.73 (CH), 135.09 (C), 135.29 (C), 141.15 (2 C), 202.85 (C=O). MS (EI): *m/z* = 298 (100), 283 (30), 255 (64), 254 (10), 253 (11), 227 (11).

(21) **4-Acetyl-3-(phenylamino)carbazole (11)**
Yellow solid; mp 153 °C. UV (MeOH): λ = 204, 242, 306, 348 (sh), 452 nm. Fluorescence (MeOH): λ_{ex} = 306 nm, λ_{em} = 411 nm. IR (ATR): ν = 3404, 2924, 2853, 1737, 1689, 1601, 1496, 1444, 1374, 1354, 1304, 1225, 1183, 1152, 1077, 1020, 903, 805, 748, 695 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.68 (s, 3 H), 6.26 (br s, 1 H), 6.85 (t, *J* = 7.4 Hz, 1 H), 6.90 (d, *J* = 8.3 Hz, 2 H), 7.18–7.23 (m, 3 H), 7.41–7.45 (m, 4 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 8.19 (br s, 1 H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 31.68 (CH_3), 110.95 (CH), 113.05 (CH), 115.90 (2 CH), 119.37 (C), 119.78 (CH), 119.80 (CH), 121.55 (C), 122.19 (CH), 122.35 (CH), 126.30 (CH), 129.33 (2 CH), 129.49 (C), 131.49 (C), 136.22 (C), 140.18 (C), 145.58 (C), 205.90 (C=O). MS (EI): *m/z* = 300 (100), 285 (67), 284 (18), 257 (48), 256 (45), 255 (30).

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(28) **Malasseziazole C (12-Formyl-5,11-dihydroindolo[3,2-*b*]carbazole-6-carboxylic Acid) (3)**
Brownish solid; mp >300 °C (decomp.). UV (MeOH): λ = 213, 247, 272 (sh), 307 (sh), 391, 465 nm. Fluorescence (MeOH): λ_{ex} = 307 nm, λ_{em} = 455 nm. IR (ATR): ν = 3448, 3055, 2922, 2852, 1712, 1611, 1585, 1512, 1458, 1392, 1347, 1321, 1299, 1263, 1205, 1158, 1126, 1077, 1022, 954, 895, 839, 804, 741, 698, 653 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 7.22 (m, 2 H), 7.48 (t, *J* = 7.6 Hz, 1 H), 7.52 (t, *J* = 7.7 Hz, 1 H), 7.79 (d, *J* = 8.2 Hz, 1 H), 7.82 (d, *J* = 8.1 Hz, 1 H), 8.58 (d, *J* = 8.2 Hz, 1 H), 8.61 (d, *J* = 8.1 Hz, 1 H), 11.41 (s, 1 H), 11.44 (s, 1 H), 11.96 (s, 1 H), 13.72 (br s, 1 H). ^1H NMR (600 MHz, CD_3OD): δ = 7.11–7.13 (m, 1 H), 7.19–7.21 (m, 1 H), 7.40–7.45 (m, 2 H), 7.60 (d, *J* = 8.0 Hz, 1 H), 7.61 (d, *J* = 7.9 Hz, 1 H), 8.33 (d, *J* = 8.0 Hz, 1 H), 8.91 (d, *J* = 8.2 Hz, 1 H), 11.50 (br s, 1 H). ^{13}C NMR and DEPT (125 MHz, DMSO-d_6): δ = 112.60 (CH), 112.72 (CH), 114.57 (C), 114.93 (C), 119.56 (CH), 119.77 (CH), 120.36 (C), 120.62 (C), 121.15 (C), 123.31 (C), 124.42 (CH), 125.09 (CH), 127.18 (CH), 127.51 (CH), 134.33 (C), 135.39 (C), 142.38 (C), 142.70 (C), 168.57 (C=O), 191.11 (CHO). ESI-MS (+25 V): *m/z* = 329.1 $[M + H]^+$.

(29) **5,11-Dihydroindolo[3,2-*b*]carbazole-6,12-dicarboxylic Acid (17)**
Red solid; mp >294 °C (decomp.). UV (MeOH): λ = 211, 275 (sh), 294, 366 nm. Fluorescence (MeOH): λ_{ex} = 294 nm, λ_{em} = 515 nm. IR (ATR): ν = 3448, 3413, 2920, 2850, 2577, 1642, 1610, 1570, 1543, 1501, 1473, 1457, 1429, 1314, 1297, 1229, 1207, 1151, 1112, 1021, 891, 857, 793, 763, 746, 699, 624 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 7.16 (m, 2 H), 7.45 (m, 2 H), 7.75 (d, *J* = 8.1 Hz, 2 H), 8.67 (d, *J* = 8.2 Hz, 2 H), 11.25 (s, 2 H), 13.95 (br s, 2 H). ^{13}C NMR and DEPT (125 MHz, DMSO-d_6): δ = 110.44 (2 C), 111.63 (2 CH), 118.31 (2 CH), 120.35 (2 C), 120.63 (2 C), 124.28 (2 CH), 126.57 (2 CH), 134.72 (2 C), 141.81 (2 C), 168.47 (2 C=O). ESI-MS (+10 V): *m/z* = 345.2 $[M + H]^+$.