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Facile zeolite induced Fischer-indole synthesis: a new approach to bioactive natural product rutaecarpine☆

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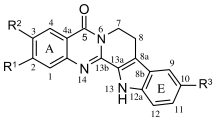
Dedicated to Dr. B. G. Hazra, OCS, NCL, Pune

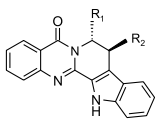
Abstract—Starting from glutaric anhydride (**5**) we have demonstrated an elegant six-step practical synthesis of bioactive natural product rutaecarpine (**1a**) via *o*-amidoglutaranilic acid formation, esterification, chemoselective ester reduction, intramolecular dehydrative cyclizations, hydrazone formation and zeolite induced Fischer-indole synthesis with 53% overall yield. The conditions employed in the present synthesis are mild, efficient and general.

1. Introduction

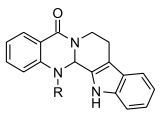
Large numbers of quinazolinone alkaloids have been isolated from a number of plants, animals and microorganisms and synthesized in view of their well established pharmacological activities.[1] Development of new, elegant synthetic routes to these bioactive quinazolinone alkaloids and their precursors is a challenging task of current interest.[2] The dried fruits of *Evodia rutaecarpa* have been used in traditional Chinese medicine under the name Wu-Chu-ru[3] and Shih-Hu[4] as a remedy for headache, dysentery, cholera, worm infections and postpartum.[5] The drug extract contains quinazolinocarboline alkaloids rutaecarpine (**1a**) and evodiamine (**3b**).[6] Recently, callus tissue cultured from the stem of *Phellodendron amurense* has been shown to produce **1a**, along with a variety of other alkaloids[7] (Fig. 1). In recent literature, **1a** and its derivatives have been reported to possess strong analgesic,[8] antiemetic,[8] astringent,[8] antihypertensive,[8] uterotonic,[9] TCDD-receptor,[10] atinociceptive,[11] anti-inflammatory[11] and cycloxygenase (COX-2) inhibitory[8] activities. The rutaecarpine (**1a**) was also found to suppress platelet plug formation in mesenteric venules and increase intracellular Ca^{2+} in endothelial cells.[12] The first total synthesis of this important bioactive natural product **1a** was reported[13] by Robinson et al. in 1927 and since then several routes to **1a** and its derivatives have been developed.[14] In our on-going studies on the synthesis of bioactive natural products using cyclic anhydrides as a potential precursors,[15] we became interested in total synthesis of rutaecarpine (**1a**). We felt that it would be possible to design the five carbon six-membered ring C



1a: $R^1 = R^2 = R^3 = H$; Rutaecarpine ($C_{18}H_{13}N_3O$, 287.32)
1b: $R^1 = R^2 = R^3 = H$; Carbon-carbon double bond between 7 and 8 position; Dehydrorutaecarpine ($C_{18}H_{11}N_3O$, 285.31)
1c: $R^1 = R^2 = H$, $R^3 = OMe$; Hortiacine ($C_{19}H_{15}N_3O_2$, 317.35)
1d: $R^1 = R^2 = -O-CH_2-O-$, $R^3 = H$; Euxylophoricine ($C_{19}H_{13}N_3O_3$, 331.33)
1e: $R^1 = R^2 = OMe$, $R^3 = H$; Euxylophoricine A ($C_{20}H_{17}N_3O_3$, 347.37)
1f: $R^1 = R^2 = R^3 = OMe$; Euxylophoricine D ($C_{21}H_{19}N_3O_4$, 377.4)



2a: $R^1 = OH$, $R^2 = H$; 7-Hydroxyrutaecarpine ($C_{18}H_{13}N_3O_2$, 303.32)
2b: $R^1 = R^2 = OH$; 7,8-Dihydroxyrutaecarpine ($C_{18}H_{13}N_3O_3$, 319.32)



3a: R = H; (13*b*,14)-Dihydrorutaecarpine ($C_{18}H_{15}N_3O$, 289.34)
3b: R = Me; Evodiamine ($C_{19}H_{17}N_3O$, 303.36)
3c: R = CHO; 14-Formyl-13*b*,14-dehydrorutaecarpine ($C_{19}H_{15}N_3O_2$, 317.35)

Figure 1. Naturally occurring bioactive rutaecarpines and analogs.

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Keywords: Glutaric anhydride; Mackinazolinone; Zeolite; Fischer indole synthesis; Rutaecarpine.
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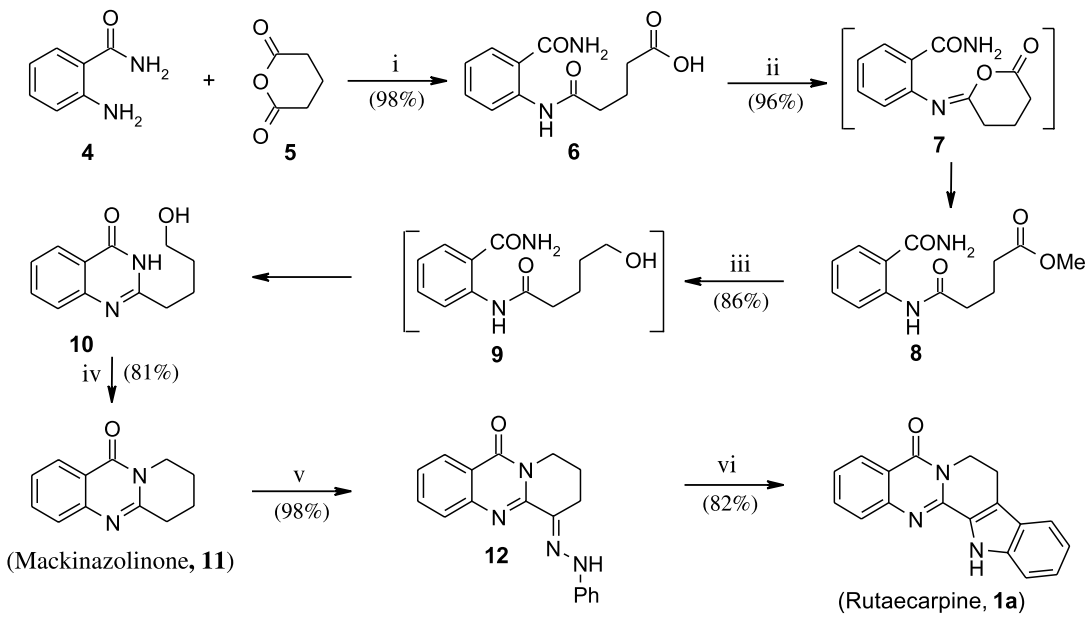

Scheme 1. Reagents, conditions and yields: (i) C_6H_6, 1,4-dioxane (2:1), room temperature, 2 h (98%); (ii) MeOH, H_2SO_4 (cat.), room temperature, 8 h (96%); (iii) $NaBH_4$, THF, reflux, 3 h, aqueous workup (86%); (iv) NaH, *p*-TsCl, THF, room temperature, 30 min (81%); (v) aniline, 30% HCl, $NaNO_2$, AcOH, −5 to 5 °C, 8 h (98%); (vi) zeolite (H-Mordenite), AcOH, reflux, 5 h (82%).

in **1a** from glutaric anhydride (**5**) and we herein report a facile six-step synthesis of **1a** (Scheme 1).

2. Results and discussion

The reaction of anthranilamide (**4**) with glutaric anhydride (**5**) in benzene/1,4-dioxane (2:1) at room temperature furnished the corresponding *o*-amidoglutaranilic acid (**6**) in quantitative yield. The glutaranilic acid **6**, on treatment with methanol and catalytic amount of sulfuric acid at room temperature, gave the corresponding methyl ester **8** in 96% yield. We feel that the present esterification at room temperature is plausibly taking place via the corresponding isoimide **7**. The ester **8** underwent smooth chemoselective sodium borohydride reduction to yield intermediate alcohol **9** which, during the aqueous work-up, underwent an in situ NaOH-catalyzed dehydrative ring closure to yield quinazolinone **10** in 86% yield. The quinazolinone **10**, on treatment with *p*-TsCl and sodium hydride in THF at room temperature, underwent a facile intramolecular dehydrative cyclization and furnished the bioactive natural product mackinazolinone (**11**) [From *Mackinalaya* species][16] in 81% yield. The analytical and spectral data obtained for **11** was in complete agreement with reported data.[16] Although several routes to **11** are known,[13,14,16] this is the first approach starting from glutaric anhydride and has several advantages. The mackinazolinone, on reaction with in situ generated diazonium salt of aniline at −5 to 5 °C, gave the corresponding hydrazone **12** in 98% yield.[14i,j] The hydrazone **12** on zeolite (H-Mordenite) induced Fischer-indole synthesis[17] in refluxing glacial acetic acid yielded the bioactive natural product rutaecarpine (**1a**) in 82% yield. The analytical and spectral data obtained for **1a** was in complete agreement with reported data.[14f,m] The overall yield of **1a** in six-steps was 53%. The rutaecarpine (**1a**) on DDQ-oxidation is known to give dehydrorutaecarpine (**1b**) in 77% yield.[14f]

3. Conclusion

In summary, starting from glutaric anhydride, we have demonstrated an elegant six-step total synthesis of bioactive natural product rutaecarpine with 53% overall yield via zeolite induced Fischer-indole synthesis. The present zeolite induced Fischer-indole synthesis conditions are mild and efficient compared to earlier known conditions and will be useful to design several naturally occurring indole skeletons. The present practical approach to quinazolinone alkaloid **1a** is efficient, general, noteworthy and can be used to design libraries of rutaecarpine analogs and derivatives.

4. Experimental

4.1. General

Melting points are uncorrected. Column chromatographic separations were carried out on ACME silica gel (60–120 mesh). Anthranilamide, glutaric anhydride, sodium borohydride, sodium hydride, *p*-toluenesulfonyl chloride and aniline were obtained from Aldrich Chemical Co. Zeolite H-Mordenite was obtained from PQ Zeolites (Netherlands) and was heated at 500 °C for 6 h before using.

4.1.1. *o*-Amidoglutaranilic acid (6). To a solution of glutaric anhydride (**5**, 2.28 g, 20 mmol) in benzene (50 mL) was added a solution of anthranilamide (**4**, 2.72 g, 20 mmol) in 1,4-dioxane (25 mL), in a dropwise fashion with constant stirring at room temperature. Reaction mixture was further stirred for 2 h and the formed precipitate was filtered in vacuo and washed with benzene (2×25 mL). The obtained compound **6** was used for the next step without any further purification. Analytically pure **6** was obtained by recrystallization from ethyl acetate.

Compound **6**. 4.90 g (98% yield); crystalline solid; mp 131–133 °C (ethyl acetate); ^{1}H NMR (CD_3OD, 300 MHz) δ 2.01 (quintet, J=9 Hz, 2H), 2.42 (t, J=9 Hz, 2H), 2.49 (t, J=9 Hz, 2H), 7.16 (t, J=9 Hz, 1H), 7.50 (t, J=9 Hz, 1H), 7.75 (d, J=9 Hz, 1H), 8.41 (d, J=9 Hz, 1H); ^{13}C NMR (CD_3OD, 75 MHz) δ 21.9, 34.1, 37.9, 122.2, 122.6, 124.4, 129.4, 133.4, 140.2, 173.5, 173.6, 176.7; IR (Nujol) ν_{max} 3449, 3317, 3260, 2700–2500, 1688, 1680, 1634 cm^{-1}. Anal. Calcd for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.19. Found: C, 57.72; H, 5.81; N, 11.03.

4.1.2. Methyl *o*-amidoglutaranilate (8). To a solution of acid **6** (4.50 g, 18 mmol) in methanol (50 mL) was added two drops of H_2SO_4 and the reaction mixture was stirred at room temperature for 8 h. The reaction mixture was concentrated in vacuo. The residue was dissolved in ethyl acetate and washed with aqueous sodium bicarbonate solution, water, brine and the organic layer was dried over Na_2SO_4. The organic layer was concentrated in vacuo to obtain ester **8**. The obtained ester **8** was used for the next step without any further purification. Analytically pure **8** was obtained by recrystallization from benzene.

Compound **8**. 4.56 g (96% yield); crystalline solid; mp 98–100 °C (C_6H_6); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.06 (quintet, J=10 Hz, 2H), 2.43 (t, J=10 Hz, 2H), 2.47 (t, J=10 Hz, 2H), 3.68 (s, 3H), 6.15 (bs, 1H), 6.48 (bs, 1H), 7.06 (t, J=10 Hz, 1H), 7.48 (t, J=10 Hz, 1H), 7.55 (d, J=10 Hz, 1H), 8.61 (d, J=10 Hz, 1H), 11.24 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.5, 33.0, 37.1, 51.5, 118.7, 121.3, 122.5, 127.4, 133.0, 139.9, 171.0, 171.6, 173.5; IR (Nujol) ν_{max} 3337, 3273, 3179, 1740, 1680, 1678, 1616 cm^{-1}. Anal. Calcd for $C_{13}H_{16}N_2O_4$: C, 59.08; H, 6.10; N, 10.60. Found: C, 58.97; H, 6.18; N, 10.69.

4.1.3. 2-(4-Hydroxybutyl)quinazolin-4(1*H*)-one (10). To a solution of ester **8** (4.00 g, 15 mmol) in THF (50 mL) was added $NaBH_4$ (2.88 g, 76 mmol) and the reaction mixture was refluxed for 3 h under an argon atmosphere. The reaction mixture was allowed to cool to room temperature and slowly quenched with water (50 mL). The reaction mixture was further stirred for 1 h at room temperature and then acidified with acetic acid. The reaction mixture was then concentrated and dried in vacuo. The residue was stirred with THF (100 mL) for 1 h and the organic layer was filtered through celite®, dried over Na_2SO_4 and concentrated in vacuo. The obtained crude product was purified by silica gel column chromatography using a mixture of ethyl acetate and methanol (99:1) to furnish **10**.

Compound **10**. 2.84 g (86% yield); crystalline solid; mp 175–177 °C (ethyl acetate); ^{1}H NMR (CD_3OD, 500 MHz) δ 1.66 (quintet, J=10 Hz, 2H), 1.90 (quintet, J=10 Hz, 2H), 2.73 (t, J= 10 Hz, 2H), 3.63 (t, J=10 Hz, 2H), 7.50 (t, J=10 Hz, 1H), 7.65 (d, J=10 Hz, 1H), 7.80 (t, J=10 Hz, 1H), 8.19 (d, J=10 Hz, 1H); ^{13}C NMR (CD_3OD, 125 MHz) δ 25.3, 33.0, 35.9, 62.4, 121.9, 127.2, 127.3, 127.6, 135.9, 150.1, 159.6, 164.5; IR (Nujol) ν_{max} 3398, 3173, 1686, 1614, 1468 cm^{-1}. Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.04; H, 6.47; N, 12.83. Found: C, 66.11; H, 6.54; N, 12.98.

4.1.4. 6,7,8,9-Tetrahydropyrido[2,1-*b*]quinazolin-11-one (mackinazolinone, 11). To a stirred slurry of NaH (607 mg, 25.3 mmol) in THF (10 mL) was added a solution of alcohol **10** (2.5 g, 11.5 mmol) in THF (20 mL). To the above reaction mixture, a solution of *p*-toluenesulfonyl chloride (2.63 g, 14 mmol) in THF (10 mL) was added in a dropwise fashion over a period of 15 min and the reaction mixture was further stirred at room temperature for 30 min. Reaction was quenched with water (10 mL), concentrated in vacuo and extracted with ethyl acetate (100 mL). The organic layer was washed with aqueous sodium bicarbonate solution, water and brine. The organic layer was dried over Na_2SO_4 concentrated and dried in vacuo. The crude product was purified by silica gel column chromatography using a mixture of ethyl acetate and petroleum ether (1:1) to furnish **11**.

Compound **11**. 1.86 g (81% yield); crystalline solid; mp 99–101 °C (hexane) (lit.[16] mp 98.5–99.5 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.96 (quintet, J=10 Hz, 2H), 2.02 (quintet, J=10 Hz, 2H), 3.00 (t, J=10 Hz, 2H), 4.08 (t, J=10 Hz, 2H), 7.42 (t, J=10 Hz, 1H), 7.60 (d, J=10 Hz, 1H), 7.71 (t, J=10 Hz, 1H), 8.26 (d, J=10 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.2, 22.0, 31.7, 42.2, 120.3, 125.9, 126.2, 126.5, 134.0, 147.2, 154.8, 162.0; IR (Nujol) ν_{max} 1657, 1612, 1587, 1566, 1462 cm^{-1}. Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 72.08; H, 6.19; N, 14.12.

4.1.5. 6-Phenylhydrazono-6,7,8,9-tetrahydro-11*H*-pyrido-[2,1-*b*]quinazolin-11-one (12). Phenyldiazonium chloride was prepared from aniline (512 mg, 5.5 mmol) in 20% hydrochloric acid (5 mL) at 0 °C using a solution of sodium nitrite (380 mg, 5.5 mmol) in water (5 mL). The reaction mixture was diluted with acetic acid (5 mL) and then was adjusted to pH 4 using sodium acetate. To this solution of phenyldiazonium chloride was added dropwise a solution of the quinazolinone **11** (1.00 g, 5.0 mmol) in 50% acetic acid (10 mL) at 0 °C over a period of 15 min. The reaction mixture was further stirred at 0 °C for 3 h and then allowed to stand overnight in a refrigerator. The precipitated crystalline compound was filtered off, washed with water, dried in vacuo to obtain pure **12**.

Compound **12**. 1.50 g (98% yield); yellow crystalline solid; mp 184–186 (PrOH) (lit.[14j] mp 182–184 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.06 (quintet, J=10 Hz, 2H), 2.79 (t, J=10 Hz, 2H), 4.02 (t, J=5 Hz, 2H), 6.89 (t, J=10 Hz, 1H), 7.20 (d, J=10 Hz, 2H), 7.25 (t, J=10 Hz, 2H), 7.39 (t, J=10 Hz, 1H), 7.57 (d, J=10 Hz, 1H), 7.68 (t, J=10 Hz, 1H), 8.20 (d, J=10 Hz, 1H), 14.56 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 31.0, 43.0, 113.5, 120.2, 121.6, 124.0, 126.3, 126.6, 126.9, 129.2, 134.1, 143.7, 145.5, 147.3, 161.3; IR ($CHCl_3$) ν_{max} 3018, 1670, 1607 cm^{-1}. Anal. Calcd for $C_{18}H_{16}N_4O$: C, 71.03; H, 5.30; N, 18.41. Found: C, 70.89; H, 5.41; N, 18.66.

4.1.6. 8,13-Dihydroindolo[2′,3′:3,4]pyrido[2,1-*b*]quinazolin-5(7*H*)-one (rutaecarpine, 1a). To a solution of hydrazone **12** (500 mg, 1.65 mmol) in freshly distilled glacial acetic acid (10 mL) was added zeolite H-Mordenite (2 g) and the stirred reaction mixture was refluxed for 5 h under argon atmosphere. Acetic acid was distilled off in vacuo and the residue was dried to the pump and then stirred with THF (50 mL) for 1 h. The above reaction mixture was

filtered and dried over Na_2SO_4. The organic layer was concentrated in vacuo and the obtained crude product was purified by silica gel column chromatography using a mixture of ethyl acetate and methanol (98:2) to furnish **1a**.

Compound **1a**. 387 mg (82% yield); crystalline solid; mp 257–259 °C (ethyl acetate) (lit.[14j] mp 258 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.15 (t, J=10 Hz, 2H), 4.51 (t, J=10 Hz, 2H), 7.09 (t, J=10 Hz, 1H), 7.17–7.28 (m, 2H), 7.34 (t, J=10 Hz, 1H), 7.52–7.64 (m, 3H), 8.25 (d, J=10 Hz, 1H), 9.62 (bs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.7, 41.2, 112.1, 118.5, 120.1, 120.6, 121.2, 125.6 (2-carbons), 126.2, 126.5, 127.1, 127.3, 134.3, 138.4, 145.1, 147.4, 161.5; IR ($CHCl_3$) ν_{max} 3416, 1670, 1651, 1630, 1599 cm^{-1}. Anal. Calcd for $C_{18}H_{13}N_3O$: C, 75.25; H, 4.56; N, 14.63. Found: C, 75.31; H, 4.67; N, 14.72.

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