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FORMATION AND REACTION OF *o*-QUINOL ACETATES OF *N*-ACYL- AND *N*-METHANESULFONYL-1,2,3,4-TETRAHYDRO-6-METHOXYISOQUINOLIN-7-OLS‡

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Abstract - Oxidation of *N*-formyl-, *N*-acetyl-, *N*-ethoxycarbonyl-, and *N*-methanesulfonyl-1,2,3,4-tetrahydro-6-methoxyisoquinolin-7-ols (**1b-e**) with lead tetraacetate in dichloromethane ($CH2Cl_2$) produced quantitatively corresponding *o*-quinol acetates (**2b-e**), treatment of which with trifluoroacetic acid in CH_2Cl_2 at 0°C for a few minutes afforded corresponding *N*-acyl- and *N*-methanesulfonyl-wilsonirines (**4b-e**) and *N*-acyl- and *N*-methanesulfonylnorsebiferines (**5b-e**). When the reaction was carried out at room temperature, *o*-quinol acetates (**2d**,**e**) of *N*-ethoxycarbonyl and *N*-methanesulfonyl congeners (**1d,e**) gave 1-[2-(ethoxycarbonylamino)ethyl]- and 1-[2-(methanesulfonylamino)ethyl]-4-hydroxy-3,6,7-trimethoxyphenanthrenes (**8d,e**).

Oxidation of 1-arylalkyl-*N*-methyl-1,2,3,4-tetrahydroisoquinolinols with lead tetraacetate (LTA) followed by the acid treatment has been extensively studied in our labolatory[1] to explore the novel methodology for synthesis of isoquinoline alkaloids. However, formation of morphinandienones from *N*-methyl-1,2,3,4-tetrahydroisoquinolinols by the methodology has been unsuccessful. Furthermore, a series of reactions have been investigated, and we have found that oxidation of *N*-trifluoroacetyl-1,2,3,4-tetrahydro-6-

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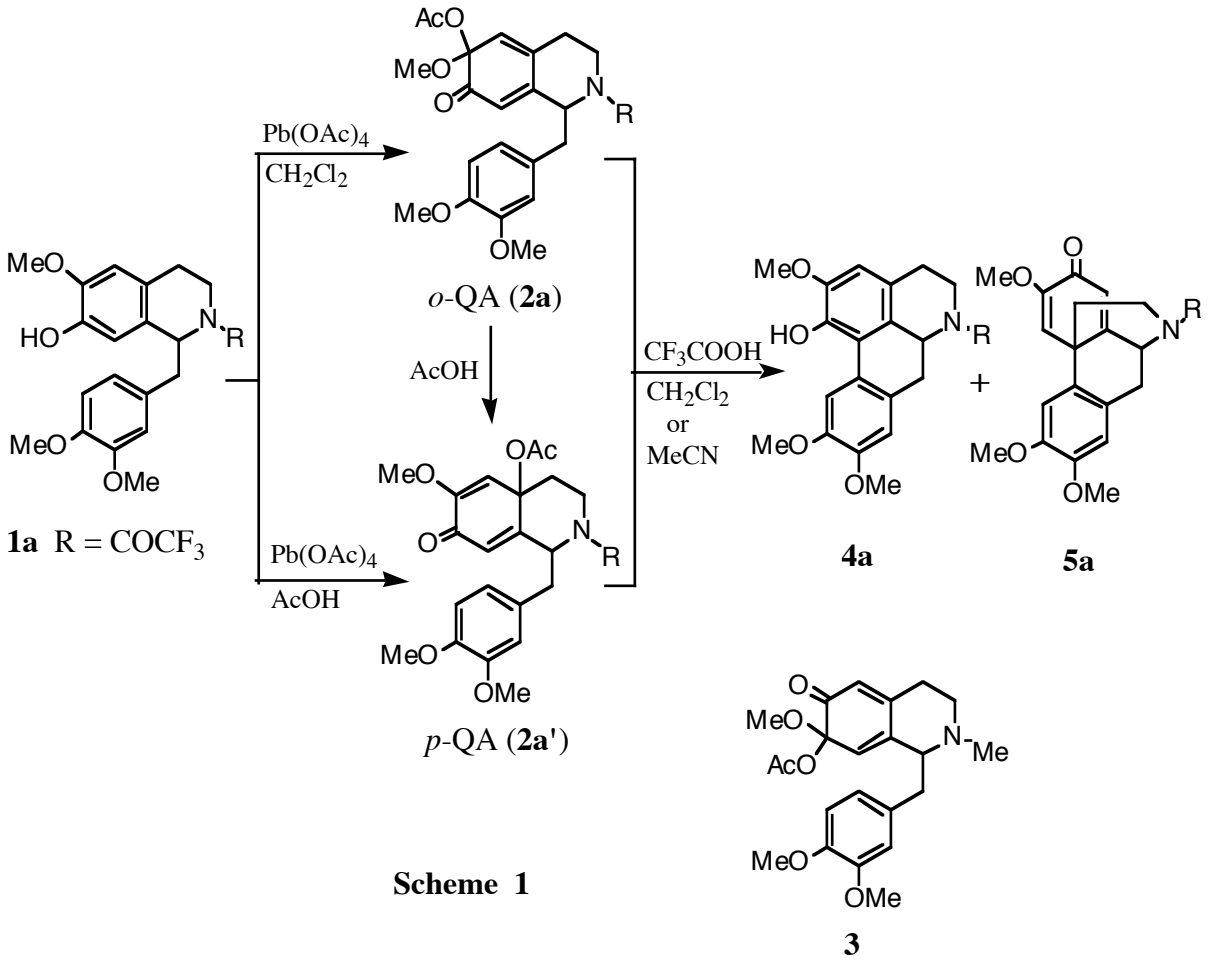
‡ This paper is dedicated to Professor Teruaki Mukaiyama, Science University of Tokyo, on the occasion of his 73rd birthday.

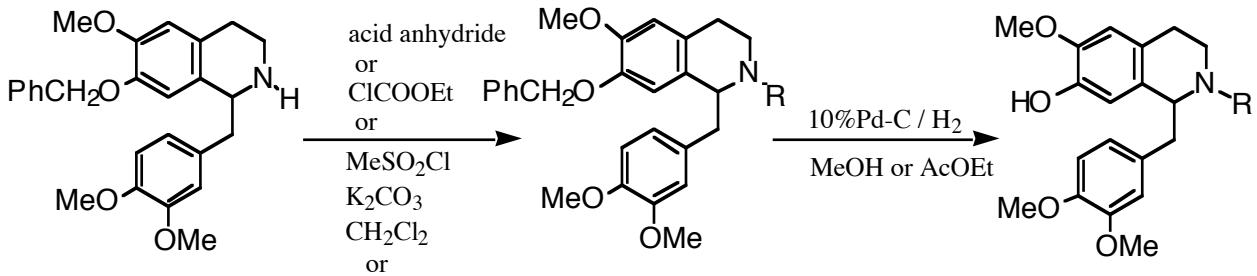
methoxyisoquinolin-7-ol (**1a**) with LTA in dichloromethane (CH_2Cl_2) or acetic acid (AcOH) gives rise to the corresponding *o*- (**2a**)[2a,b] or *p*- (**2a'**)[2c] quinol acetate (QA) (*p*-QA is also formed by treatment of *o*-QA with AcOH), which is treatedwith trifluoroacetic acid (TFA) in CH_2Cl_2 or MeCN at low temperatrure to produce *N*-trifluoroacetylwilsonirine (**4a**)[3] and *N*-trifluoroacetylnorsebiferine (**5a**)[3] (Scheme 1).



Scheme 1

This findings prompted us to examine a series of reactions on some *N*-acyl-1,2,3,4-tetrahydroisoquinolin-7-ols, because it should constitute one of the methods for synthesis of isoquinoline alkaloids. The present paper deals with formation and reaction of *o*-QAs (**2b-e**) of *N*-acyl- and *N*-methanesulfonyl-1,2,3,4-tetrahydroisoquinolin-7-ols (**1b-e**).

Starting materials (**1b-e**) were prepared as follows. *N*-Acylation or *N*-methanesulfonylation of **6**[4] was performed by treatment with ethyl formate, acid anhydride, ethyl chloroformate or methanesulfonyl chloride under basic conditions (except for **1b**) to give **7b-e** in good yields. Debenzylation of **7b-e** by catalytic hydrogenation produced *N*-acyl- and *N*-methanesulfonyl-1,2,3,4-tetrahydroisoquinolin-7-ols (**1b-e**) (Scheme 2).



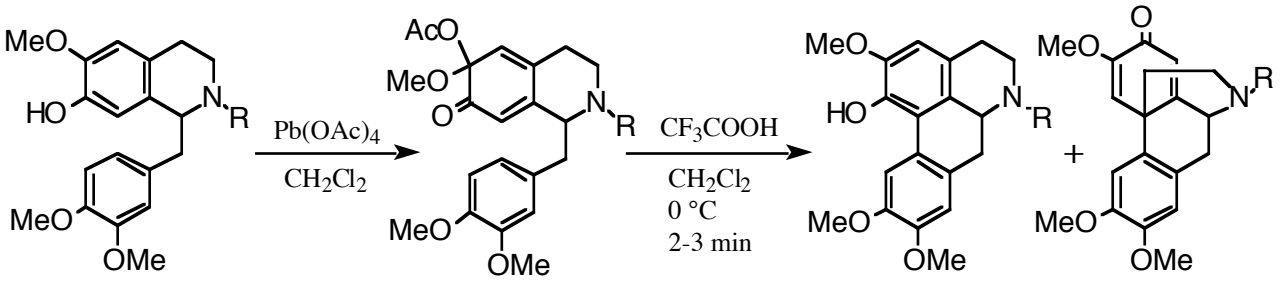
6

7b R = CHO
c R = Ac
d R = COOEt
e R = SO_2Me

1b R = CHO
c R = Ac
d R = COOEt
e R = SO_2Me

Scheme 2

LTA oxidation of **1b-e** in a manner similar to that reported previously[2a] produced in quantitative yields *N*-acyl and *N*-methanesulfonyl *o*-QAs (**2b-e**) as an oil, which were stable at room temperature, compared with *N*-methyl *o*-QA (**3**).[5,6] Structures of *o*-QAs (**2b-e**) were confirmed by their spectral evidence (see EXPERIMENTAL).



1b R = CHO
c R = Ac
d R = COOEt
e R = SO_2Me

2b R = CHO
c R = Ac
d R = COOEt
e R = SO_2Me

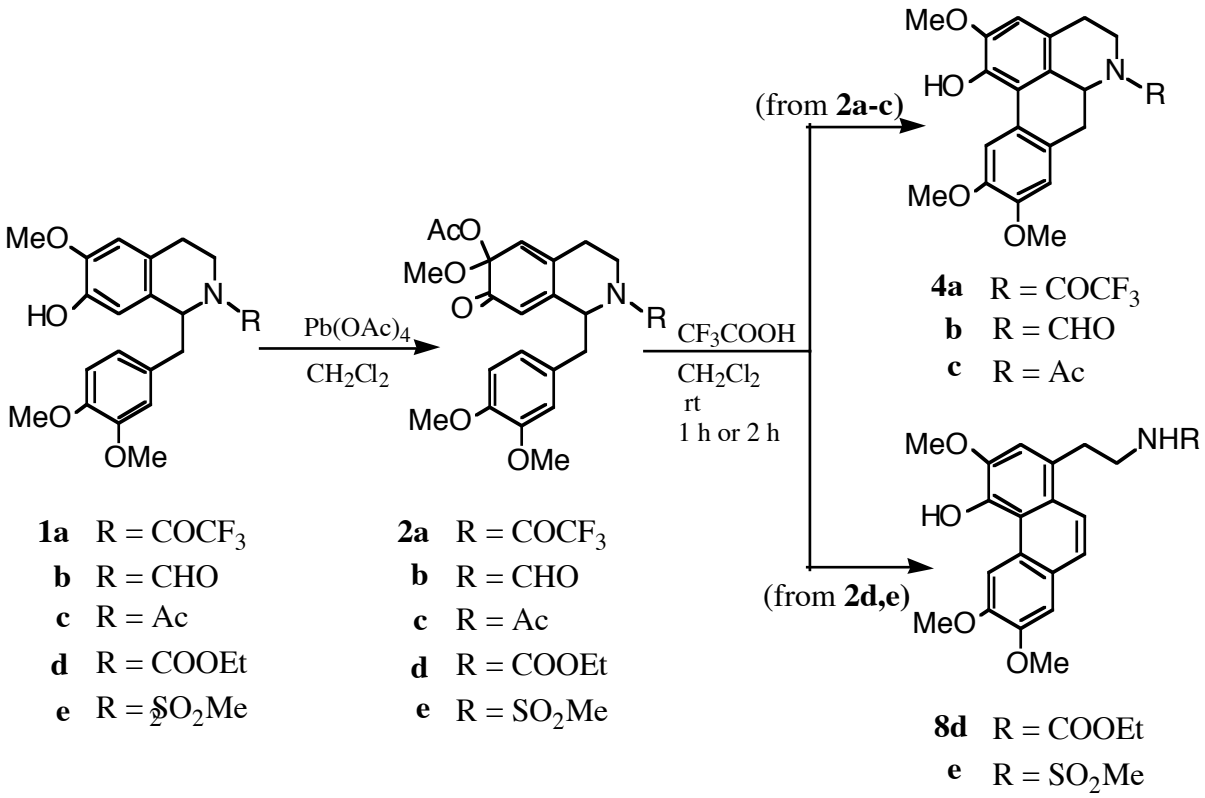
4b R = CHO
c R = Ac
d R = COOEt
e R = SO_2Me

5b R = CHO
c R = Ac
d R = COOEt
e R = SO_2Me

Scheme 3

The reaction of *o*-QAs (**2b-e**) thus obtained with TFA in CH_2Cl_2 at 0 °C for a few minutes produced on purification by preparative TLC *N*-acyl- and *N*-methanesulfonylwilsonirines (**4b-e**) and *N*-acetyl- and *N*-methanesulfonylnorsebiferines (**5b-e**) in moderate yields, regardless of the nature of *N*-acyl groups in *o*-QAs (Scheme 3). Structures of **4b-e** and **5b-e** were proved by their spectral evidence (see EXPERIMENTAL).

Interestingly, however, the analogous reaction of **2a-c** at room temperature for 2 h (1 h for **2a**) afforded *N*-acylwilsonirines (**4a-c**) as a sole product, while that of **2d**,**e** produced phenanthrene derivatives (**8d, e**),[7] which were formed by cyclization of **2d**,**e** to *N*-ethoxycarbonyl- and *N*-methanesulfonylwilsonirines (**4d,e**) followed by cleavage of a 6-6a bond in **4d**,**e** (Scheme 4).



Scheme 4

It is noteworthy[8,9] that the reaction of *N*-ethoxycarbonyl- and *N*-methanesulfonylnoraporphines (**4d,e**) with TFA-CH_2Cl_2 readily proceeded at room temperature to give the corresponding phenanthrene derivatives (**8d,e**). The present reaction would be explainable by considering that an inductive effect of ethoxycarbonylamino and methanesulfonylamino groups is more effective than that of acylamino groups. In conclusion, it was proved that LTA oxidation of *N*-acyl- and *N*-methanesulfonyltetrahydroisoquinolin-7-ols in CH_2Cl_2 gave stable *o*-QAs, TFA treatment of which afforded *N*-acylnoraporphines and *N*-acylnormorphinandienones without regard to the nature of *N*-acyl groups, when it was carried out at 0 °C for a few minutes.

EXPERIMENTAL

All melting points were measured on a Büchi melting point measuring apparatus and are uncorrected. ^{1}HNMR spectra were recorded on a JOEL JNM-FX 100 (100 MHz) instrument in $CDCl_3$ solution using TMS as internal standard. IR spectra were taken on a Hitachi 260-10 spectrophotometer in $CHCl_3$ solution. MS spectra were run with a Hitachi RMU-7M or M-80 instrument. Preparative TLC was performed on Merck Kieselgel $60F_{254}$ plates (20 x 20 x 0.5 cm).

Preparation of *N*-Acyl- and *N*-methanesulfonyl-1-(3,4-dimethoxy)benzyl-1,2,3,4-tetrahydro-6-methoxy-7-phenylmethoxyisoquinolines (7b-e)

A mixture of **6**,[4] ethyl formate, acid anhydride, ethyl chloroformate or methanesulfonyl chloride and K_2CO_3, pyridine, or triethylamine in CH_2Cl_2 or without solvent was stirred at rt (except for **7b**). After addition of water to the reaction mixture, the product was taken up in CH_2Cl_2. Usual work-up of the organic layer gave a solid, which was purified by recrystallization (except for **7b**).

N-Formyl-1,2,3,4-tetrahydro-6-methoxy-1-(3,4-dimethoxy)benzyl-7-phenylmethoxyisoquinoline (**7b**): a solution of **6** (0.9 g, 2.4 mmol) in ethyl formate (20 mL) was refluxed for 2 h. Removal of the solvent *in vacuo* gave an oil, which was crystallized by trituration in hexane to give **7b** (0.63 g, 98%), mp 44-48 °C. MS *m/z*: 448 $(MH)^+$; IR ν: 1650 cm^{-1}; ^{1}H NMR δ: 3.70, 3.82, 3.84, 3.86 (9H, each s), 4.92, 4.94, 5.08 (2H, each s), 5.24-5.48 (2H, m), 6.20-6.82 (3H, m), 7.00-7.48 (5H, m), 7.64, 8.08 (1H, each s).

N-Acetyl-1,2,3,4-tetrahydro-6-methoxy-1-(3,4-dimethoxy)benzyl-7-phenylmethoxyisoquinoline (**7c**): **6** (1.0 g, 2.4 mmol), acetic anhydride (10 mL, 106 mmol), and pyridine (10 mL, 124 mmol) were used (the reaction time: 4 d); **7c** (0.89 g, 81%), mp 108-109 °C (EtOH). Anal Calcd for $C_{28}H_{31}NO_5$: C, 72.86; H, 6.77; N, 3.03. Found: C, 72.91; H, 6.86; N, 3.18. MS *m/z*: 461 (M^+); IR ν: 1620 cm^{-1}; ^{1}H NMR δ: 1.60, 2.12 (3H, each s), 3.72, 3.82, 3.83, 3.84, 3.85 (9H, each s), 4.85, 4.88, 5.05 (2H, each s), 6.22-6.84, 7.08-7.48 (each 5H, m).

[3]

N-Ethoxycarbonyl-1,2,3,4-tetrahydro-6-methoxy-1-(3,4-dimethoxy)benzyl-7-phenylmethoxyisoquinoline (**7d**): **6** (1.08 g, 2.6 mmol), ethyl chloroformate (0.56 g, 5.2 mmol), K_2CO_3 (0.71 g, 5.2 mmol), and CH_2Cl_2 (20 mL) were used (the reaction time: 1 h). **7d** (1.03 g, 81.7%), mp 99-101 °C (EtOH). Anal Calcd for $C_{29}H_{33}NO_6$: C, 70.86; H, 6.77; N, 2.85. Found: C, 70.78; H, 6.89; N, 2.89. MS *m/z*: 491 (M^+); IR ν: 1670 cm^{-1}; ^{1}H NMR δ: 1.12, 1.24 (3H, each t, *J* = 7.1 Hz), 3.76, 3.82, 3.83 (9H, each s), 4.67-5.23 (3H, m), 6.12-6.80, 7.02-7.44 (each 5H, m).

1,2,3,4-Tetrahydro-N-methanesulfonyl-6-methoxy-1-(3,4-dimethoxy)benzyl-7-phenylmethoxy-isoquinoline (**7e**): **6** (1.0 g, 2.4 mmol), methanesulfonyl chloride (1.9 mL, 11.4 mmol), K_2CO_3 (3.37 g,

2.4 mmol), and CH_2Cl_2 (20 mL) were used (the reaction time: 1.5 h); **7e** (1.02 g, 86%), mp 136-137 °C (MeOH). Anal Calcd for $C_{27}H_{31}NO_6S$: C, 65.17; H, 6.28; N, 2.81; S, 6.43. Found: C, 65.23; H, 6.38; N, 2.94; S, 6.42. MS *m/z*: 497 (M^+); IR ν: 1320, 1140 cm^{-1}; ^1H NMR δ: 2.48 (3H, s), 3.79, 3.83, 3.84 (9H, each s), 4.76-5.08 (3H, m), 6.28-6.82, 7.02-7.42 (each 5H, m).

Preparation of *N*-Acyl- and *N*-methanesulfonyl-1,2,3,4-tetrahydro-6-methoxy-1-(3,4-dimethoxy)benzylisoquinolin-7-ols (1b-e)

A mixture of **7b-e**, 2% aqueous $PdCl_2$ solution and carbon in MeOH (for **7b, c**) or 10% Pd-C in AcOEt (for **7d, e**) was shaken with hydrogen (1 atm) at rt. After filtration of catalyst followed by removal of the solvent *in vacuo* gave a solid, purification of which was performed by recrystallization.

N-Formyl-1,2,3,4-tetrahydro-6-methoxy-1-(3,4-dimethoxy)benzylisoquinolin-7-ol (**1b**): **7b** (1.3 g, 2.9 mmol), 2% aqueous $PdCl_2$ solution (3 mL), carbon (0.37 g), and MeOH (15 mL) were used (the reaction time: 4 h); **1b** (0.58 g, 92%), mp 180-182 °C (benzene). Anal Calcd for $C_{20}H_{23}NO_5$: C, 67.21; H, 6.49; N, 3.92. Found: C, 67.29; H, 6.52; N, 4.06. MS *m/z*: 358 $(MH)^+$; IR ν: 3510, 1645 cm^{-1}; ^1H NMR δ: 3.70, 3.80, 3.83, 3.86 (9H, each s), 4.24-4.60, 5.36-5.56 (2H, each m), 6.30-6.84 (5H, m), 7.56, 8.05 (1H, each s).

N-Acetyl-1,2,3,4-tetrahydro-6-methoxy-1-(3,4-dimethoxy)benzylisoquinolin-7-ol (**1c**): **7c** (0.87 g, 1.9 mmol), 2% aqueous $PdCl_2$ solution (3.5 mL), carbon (0.6 g), and MeOH (15 mL) were used (the reaction time: 4 h); **1c** (0.53 g, 75%), mp 141-142 °C (EtOH). Anal. Calcd for $C_{21}H_{25}NO_5$: C, 67.91; H, 6.78; N, 3.77. Found: C, 67.88; H, 6.74; N, 3.85. MS *m/z*: 371 (M^+); IR ν: 3525, 1620 cm^{-1}; ^1H NMR δ: 1.52, 2.11 (3H, each s), 3.72, 3.83, 3.84, 3.85, 3.87 (9H, each s), 6.40-6.60 (5H, m).

N-Ethoxycarbonyl-1,2,3,4-tetrahydro-6-methoxy-1-(3,4-dimethoxy)benzylisoquinolin-7-ol (**1d**): **7d** (0.84 g, 1.7 mmol), 10% Pd-C (0.36 g), and AcOEt (40 mL) were used (the reaction time: 3 h); **1d** (0.58 g, 84%), mp 162-164 °C (ether). Anal Calcd for $C_{22}H_{27}NO_6$: C, 65.82; H, 6.78; N, 3.49. Found: C, 65.85; H, 6.82; N, 3.48. MS *m/z*: 401 (M^+); IR ν: 3450, 1670 cm^{-1}; ^1H NMR δ: 1.12, 1.24 (3H, each t, *J* = 7.1 Hz), 3.79, 3.83, 3.85 (9H, each s), 4.14 (2H, q, *J* = 7.1 Hz), 5.14 (1H, dd, *J* = 7.1, 12.9 Hz), 6.36-6.86 (5H, m).

1,2,3,4-Tetrahydro-N-methanesulfonyl-6-methoxy-1-(3,4-dimethoxy)benzylisoquinolin-7-ol (**1e**): **7e** (1.31 g, 2.6 mmol), 10% Pd-C (0.56 g), and AcOEt (40 mL) were used (the reaction time: 3 h); **1e** (0.95 g, 89%), mp 153-155 °C (benzene). Anal Calcd for $C_{20}H_{25}NO_6S$: C, 58.95; H, 6.18; N, 3.44; S, 7.87. Found: C, 59.21; H, 6.16; N, 3.54; S, 7.83. MS *m/z*: 407 (M^+); IR ν: 3520, 1320, 1140 cm^{-1}; ^1H NMR

δ: 2.41 (3H, s), 3.81, 3.84, 3.86 (each 3H, s), 4.94 (1H, t, J = 7.1 Hz), 6.44-6.80 (5H, m).

Formation of 6-Acetoxy-*N*-acyl- and 6-Acetoxy-*N*-methanesulfonyl-1,2,3,4,6,7-hexahydro-6-methoxy-1-(3,4-dimethoxy)benzyl-7-oxoisoquinolines (2b-e) (*o*-Quinol Acetates)

The reaction of **1b-e** with $Pb(OAc)_4$ in CH_2Cl_2 was carried out in a manner reported previously[2a] (the reaction time: 0.5 h) to produce *o*-quinol acetates (*o*-QAs) (**2b-e**) quantitatively**.** They were used in the next reaction without further purification.

7-Acetoxy-N-formyl-1,2,3,4,6,7-hexahydro-6-methoxy-1-(3,4-dimethoxy)benzyl-7-oxoisoquinoline (**2b**)**: 1b** (100 mg, 0.28 mmol), $Pb(OAc)_4$ (150 mg, 0.34 mmol), and CH_2Cl_2 (3 mL) were used. **2b** (oil)**;** IR ν: 1725, 1655 cm^{-1}; ^1H NMR δ: 2.09, 2.10, 2.12 (3H, each s), 3.42, 3.43, 3.44, 3.46 (3H, each s), 3.83 (6H, s), 5.00-5.32 (1H, m), 7.62, 7.69, 8.08, 8.10 (1H, each s).

6-Acetoxy-N-acetyl-1,2,3,4,6,7-hexahydro-6-methoxy-1-(3,4-dimethoxy)benzyl-7-oxoisoquinoline (**2c**)**:** **1c** (100 mg, 0.27 mmol), $Pb(OAc)_4$ (143 mg, 0.32 mmol), and CH_2Cl_2 (1 mL) were used. **2c** (oil)**;** IR ν: 1730, 1680, 1625 cm^{-1}; ^1H NMR δ: 2.08, 2.10, 2.12, 2.13 (6H, each s), 3.41 (3H, s), 3.83, 3.84 (each 3H, s), 5.41, 5.71, 5.74 (1H, each s), 5.92-6.06 (1H, m), 6.50-6.84 (3H, m).

6-Acetoxy-N-ethoxycarbonyl-1,2,3,4,6,7-hexahydro-6-methoxy-1-(3,4-dimethoxy)benzyl-7-oxoisoquinoline (**2d**)**: 1d** (100 mg, 0.25 mmol), $Pb(OAc)_4$ (133 mg, 0.30 mmol), and CH_2Cl_2 (1 mL) were used. **2d** (oil)**;** IR ν: 1725, 1670 cm^{-1}; ^1H NMR δ: 1.26, 1.28 (3H, each t, *J* = 7.1 Hz), 2.09, 2.10 (3H, each s), 3.42 (3H, s), 3.82, 3.84, 3.85 (6H, each s), 4.68-5.00, 5.33-5.56 (each 1H, m), 5.96 (1H, s), 6.48-6.88 (3H, m).

6-Acetoxy-1,2,3,4,6,7-hexahydro-N-methanesulfonyl-6-methoxy-1-(3,4-dimethoxy)benzyl-7-oxoisoquinoline (**2e**)**:** **1e** (100 mg, 0.25 mmol), $Pb(OAc)_4$ (143 mg, 0.32 mmol), and CH_2Cl_2 (1 mL) were used. **2e** (oil); IR ν: 1735, 1680, 1325, 1140 cm^{-1}; ^1H NMR δ: 2.08, 2.10 (3H, each s), 2.57, 2.66 (3H, each s), 3.42, 3.44 (3H, each s), 3.84 (6H, s), 4.66 (1H, dd, *J* = 7.1, 12.9 Hz), 5.50-5.58 (1H, each s), 5.90-6.04 (1H, m), 6.50-6.84 (3H, m).

The Reaction of *o*-QAs (2) with CF_3COOH in CH_2Cl_2.

A solution of *o*-QAs (**2**) (prepared from **1** as noted above) in CF_3COOH- CH_2Cl_2 was stirred at 0 °C for 3 min (2 min for **2e**) or at rt for 2 h (1 h for **2a**). The reaction mixture was basified with 10% aqueous Na_2CO_3 solution. The product was taken up in CH_2Cl_2. A residue obtained on usual work-up of the organic layer was purified by preparative TLC (developing solvent: AcOEt : hexane = 2 : 1).

From **1a**[3]: At rt: **2a**[2a,b] [prepared from **1a** (100 mg)], CF_3COOH (5 mL), and CH_2Cl_2 (5 mL) were used. *N-Trifluoroacetylwilsonirine* (**4a**, 61 mg, 61%) was obtained. It was identical in all respects with the authentic sample.[2c]

From **2b**: (1) At 0 °C: **2b** [prepared from **1b** (200 mg)], CF_3COOH (1 mL), and CH_2Cl_2 (20 mL) were used. *N-Formylwilsonirine* (**4b**, 120 mg, 60%), mp 148-149 °C (CH_2Cl_2-hexane): HRMS *m/z*: Calcd for $C_{20}H_{21}NO_4$ (M^+): 355.1418. Found: 355.1416. IR ν: 1650 cm^{-1}; ^1H NMR δ: 3.90, 3.92 (9H, each s), 4.94 (1H, dd, *J* = 4.3, 14.3 Hz), 6.52, 6.55 (1H, each s), 6.72, 6.76 (1H, each s), 8.05 (1H, s), 8.21, 8.35 (1H, each s). *N-Formylnorsebiferine* (**5b**, 16 mg, 8%), mp 136 °C (ether): MS *m/z*: 355 (M^+); IR ν: 1670, 1650, 1620 cm^{-1}; ^1H NMR δ: 3.80, 3.85, 3.90 (each 3H, s), 6.31 (1H, s), 6.34, 6.38 (1H, each s), 6.58, 6.82 (each 1H, s), 8.02, 8.18 (1H, each s).

(2) At rt: **2b** [prepared from **1b** (100 mg)], CF_3COOH (1 mL), and CH_2Cl_2 (20 mL) were used. *N-Formylwilsonirine* (**4b**, 67.2 mg, 68%) was obtained. It was identical in all respects with the product obtined in (1).

From **2c**: (1) At 0 °C: **2c** [prepared from **1c** (200 mg)], CF_3COOH (1 mL), and CH_2Cl_2 (20 mL) were used. *N-Acetylwilsonirine* (**4c**, 132 mg, 66%), mp 121-126 °C (MeOH): Anal Calcd for $C_{21}H_{23}NO_5$•MeOH: C, 65.82; H, 6.78; N, 3.49. Found: 65.63; H, 6.70; N, 3.48. IR ν: 3570, 1620 cm^{-1}; ^1H NMR δ: 2.20 (3H, s), 3.91 (9H, s), 6.54, 6.73, 8.07 (each 1H, s). *N-Acetylnorsebiferine* (**5c**, 40.6 mg, 20%), mp 156-159 °C (ether): MS *m/z*: 369 (M^+); IR ν: 1680, 1650, 1630 cm^{-1}; ^1H NMR δ: 2.03, 2.24 (3H, each s), 3.80, 3.84, 3.90 (9H, each s), 6.40-6.50 (2H, m), 6.58, 6.82 (each 1H, s).

(2) At rt: **2c** [prepared from **1c** (100 mg)], CF_3COOH (1 mL), and CH_2Cl_2 (20 mL) were used. *N-Acetylwilsonirine* (**4c**, 62.4 mg, 63%) was obtained. It was identical in all respects with the product obtined in (1).

From **2d**: At 0 °C: **2d** [prepared from **1d** (100 mg)], CF_3COOH (0.5 mL), and CH_2Cl_2 (10 mL) were used. *N-Ethoxycarbonylwilsonirine* (**4d**, 80.4 mg, 81%), mp 116-125 °C (ether-hexane): Anal Calcd for $C_{22}H_{22}NO_6$•H_2O: C, 63.31; H, 6.53; N, 3.36. Found: 63.49; H, 6.61; N, 3.33. MS *m/z*: 399 (M^+); IR ν: 3500, 1675 cm^{-1}; ^1H NMR δ: 3.91, 3.92 (9H, each s), 4.75 (1H, dd, *J* = 5.7, 12.9 Hz), 6.12, 6.56, 6.74, 6.76, 8.05 (each 1H, s). *N-Ethoxycarbonylnorsebiferine* (**5d**, 15.2 mg, 15%), mp 135-137 °C (ether-hexane): Anal Calcd for $C_{22}H_{25}NO_6$: C, 66.15; H, 6.31; N, 3.51. Found: C, 66.09; H, 6.11; N, 3.51. MS *m/z*: 399 (M^+); IR ν: 1670, 1645, 1620 cm^{-1}; ^1H NMR δ: 3.79, 3.84, 3.88 (9H, each s), 6.33 (2H, s), 6.34, 6.38 (1H, each s), 6.57, 6.80 (each 1H, s).

(2) At rt: **2d** [prepared from **1d** (100 mg)], CF_3COOH (0.5 mL), and CH_2Cl_2 (10 mL) were used. *1-[2-(Ethoxycarbonylamino)ethyl]-4-hydroxy-3,6,7-trimethoxyphenanthrene* (**8d**, 63.8 mg, 64%), mp 145-146 °C (MeOH): Anal Calcd for $C_{22}H_{25}NO_6$: C, 66.15; H, 6.31; N, 3.51. Found: C, 65.91; H, 6.32; N, 3.73. MS *m/z*: 399 (M^+); IR ν: 3440, 3360, 1710 cm^{-1}; ^1H NMR δ: 1.24 (3H, t, *J* = 7.1 Hz), 4.02, 4.07 (9H, each s), 4.12 (2H, q, *J* = 7.1 Hz), 7.07, 7.16 (1H, each s), 7.55, 7.74 (each 1H, d, *J* = 9.4 Hz), 9.25 (1H, s).

From **2e**: (1) At 0 °C: **2e** [prepared from **1e** (100 mg)], CF_3COOH (0.5 mL), and CH_2Cl_2 (10 mL) were used. *N-Methanesulfonylwilsonirine* (**4e**, 43.2 mg, 43%), mp 216-218 °C (EtOH): Anal Calcd for $C_{20}H_{23}NO_6S$: C, 59.24; H, 5.72; N, 3.45; S, 7.89. Found: C, 59.19; H, 5.66; N, 3.45; S, 8.06. MS *m/z*: 405 (M^+); IR ν: 3520, 1310, 1140 cm^{-1}; ^1H NMR δ: 3.90, 3.92 (9H, each s), 4.54 (1H, t, *J* = 9.1 Hz), 6.16, 6.55, 6.75, 8.05 (each 1H, s). *N-Methanesulfonylnorsebiferine* (**5e**, 11 mg, 11%), mp 217-218 °C (EtOH): Anal Calcd for $C_{20}H_{23}NO_6S$: C, 59.24; H, 5.72; N, 3.45; S, 7.89. Found: C, 59.03; H, 5.63; N, 3.56; S, 8.07. MS *m/z*: 405 (M^+); IR ν: 1680, 1650, 1630, 1310, 1140 cm^{-1}; ^1H NMR δ: 3.77, 3.80, 3.86 (9H, each s), 6.62, 6.36, 6.60, 6.79 (each 1H, s).

(2) At rt: **2e** [prepared from **1e** (100 mg)], CF_3COOH (0.5 mL), and CH_2Cl_2 (10 mL) were used. *4-Hydroxy-1-[2-(methanesulfonylamino)ethyl]-3,6,7-trimethoxyphenanthrene* (**8e**, 54.2 mg, 54%), mp 190-192 °C (MeOH): Anal Calcd for $C_{20}H_{23}NO_6S$: C, 59.24; H, 5.72; N, 3.45; S, 7.89. Found: C, 59.41; H, 5.71; N, 3.48; S, 7.77. MS *m/z*: 405 (M^+); IR ν: 3510, 3410, 1310, 1145 cm^{-1}; ^1H NMR δ: 2.79 (3H, s), 4.02, 404, 4.06 (9H, each s), 7.12, 7.16 (each 1H, s), 7.50, 7.66 (each 1H, d, *J* = 8.6 Hz), 9.24 (1H, s).

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