PARTIAL DEACETYLATION OF ASTERRIQUINONE DIACETATE BY AQUEOUS SODIUM BICARBONATE IN PYRIDINE

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Asterriquinone (ARQ); 2,5-bis[1-(1,1-dimethyl-2-propenyl)-1H-indol-3-yl]-3,6-dihydroxy-2,5-cyclohexadiene-1,4-dione and ARQ monoacetate are metabolites from mycelium of Aspergillus terreus IFO 6123. ARQ diacetate was converted into ARQ monoacetate by treatment with 5% aq. NaHCO₃ in pyridine at 80°C for 5 min, and the yield was 93.4%. Similarly, by treatment with 5% aq. NaHCO₃ in acetone at room temperature, 2,5-diacetoxy-p-xyloquinone and 2,5-diacetoxy-p-benzoquinone were converted into 2-acetox-5-hydroxy-p-xyloquinone (yield, 85.8%) and 2-acetox-5-hydroxy-p-benzoquinone (yield, 66.7%), respectively.

**KEY WORDS** partial deacetylation; asterriquinone monoacetate; 2-acetox-5-hydroxy-p-xyloquinone; 2-acetox-5-hydroxy-p-benzoquinone; Aspergillus terreus IFO 6123

Asterriquinone (ARQ); 2,5-bis[1-(1,1-dimethyl-2-propenyl)-1H-indol-3-yl]-3,6-dihydroxy-2,5-cyclohexadiene-1,4-dione (IA) and ARQ monoacetate (3A) are metabolites from mycelium of Aspergillus terreus IFO 6123.¹ This prompts us to convert ARQ diacetate (2A)² into 3A by partial deacetylation. The conversion was accomplished by treatment of 2A (40.0 mg) with 5% aq. NaHCO₃ (2 ml) in pyridine (2 ml) at 80°C. After 5 min, the mixture was poured into chilled 0.1 N HCl; the resulting precipitate was purified by SiO₂ column chromatography, and 3A (34.7 mg, yield 93.4%) was afforded. By treatment with 5% aq. NaHCO₃ (2 ml) in acetone (10 ml) at 80°C for 10 min under reflux, 2A (49.4 mg) was converted into 3A (30.0 mg, yield 65.4%). Compound 3A was methylated to its methyl ether (4A),³ 4A deacetylated to ARQ monomethyl ether (5A),⁴ and 5A methylated to ARQ dimethyl ether (6A).¹

Similarly, 2,5-diacetoxy-p-xyloquinone (2B, 20.0 mg)⁵ was treated with 5% aq. NaHCO₃ (1 ml) in acetone (1 ml) at room temperature for 10 min; then the mixture was poured into chilled 0.1 N HCl, and the solution was extracted by Et₂O. Purification of the Et₂O extract by column chromatography on oxalic acid-impregnated SiO₂ gave 2-acetox-5-hydroxy-p-xyloquinone (3B, 14.3 mg, yield, 85.8%).⁶ In addition, 2,5-diacetoxy-p-benzoquinone (2C, 107.4 mg) was treated with 5% aq. NaHCO₃ (4 ml) in acetone (4 ml) at room temperature for 5 min; then the mixture was poured into chilled 0.1 N HCl and the solution extracted by Et₂O. Purification of the Et₂O extract by column chromatography on oxalic acid-impregnated SiO₂ gave 2-acetox-5-hydroxy-p-benzoquinone (3C, 58.2 mg, yield, 66.7%).⁷ The above results are shown in Chart 1.

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Reagents: (a) 1A: Ac₂O, pyridine; 1B: Ac₂O, AcONa; 1C: Ac₂O; (b) 2A: 5% aq. NaHCO₃, pyridine or acetone; 2B, 2C: 5% aq. NaHCO₃, acetone; (c) CH₂N₂ in ether; (d) 4A: 5% aq. NaHCO₃, EtOH; 4B, 4C: 5% aq. NaHCO₃.

Chart 1

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REFERENCES AND NOTES
2) 2A: blue-violet needles of mp 211-212°C (dec.) (from n-hexane). HR-EIMS: 590.2416 (Calc'd 590.2417 for C₃₆H₃₄N₂O₆). UV λ_max (EtOH) nm (log ε): 223 (4.48), 292 (4.26), 507(3.80). IR(KBr)cm⁻¹: 1778, 1670, 1594, 1226, 1184. ¹H-NMR spectrum (CDCl₃) δ: 1.83 (12H, s, 2CH(CH₃)₂CH=CH₂), 2.13 (6H, s, 2OCOCH₃), 5.25 (2H, d, J=17.6 Hz, 2CH(CH₃)₂CH=CH₂), 5.28 (2H, d, J=10.4 Hz, 2CH(CH₃)₂CH=CH₂), 6.19 (2H, dd, J=10.4, 17.6 Hz, 2CH(CH₃)₂CH=CH₂)), 7.17-7.19 (4H, m, Ar-H), 7.57-7.59 (2H, m, Ar-H), 7.65-7.67 (2H, m, Ar-H), 7.77 (2H, s, Ar-H).
3) 4A: dark purple needles of mp 195-196°C (dec.) (from n-hexane). HR-EIMS: 562.2467 (Calc'd 562.2468 for C₃₅H₃₄N₂O₅). UV λ_max (EtOH) nm (log ε): 223(4.68), 291 (4.44), 496 (3.89). IR (KBr) cm⁻¹: 1776, 1666, 1596, 1192. ¹H-NMR spectrum (CDCl₃) δ: 1.83 (6H, s, C(CH₃)₂CH=CH₂), 1.84 (6H, s, C(CH₃)₂CH=CH₂), 2.13 (3H, s, OOCOCH₃), 3.74 (3H, s, OCH₃), 5.23 (1H, d, J=17.6 Hz, C(CH₃)₂CH=CH₂), 5.25 (1H, d, J=17.6 Hz, C(CH₃)₂CH=CH₂), 5.26 (1H, d, J=17.6 Hz,
C(\(\text{CH}_3\))_2\text{CH}=\text{CH}_2\text{)}, 5.29 (1H, d, J=10.4 Hz, C(\(\text{CH}_3\))_2\text{CH}=\text{CH}_2\text{)}, 6.20 (2H, dd, J=10.4, 17.6 Hz, 2C(\(\text{CH}_3\))_2\text{CH}=\text{CH}_2\text{)}, 7.15-7.18 (4H, m, Ar-H), 7.56-7.65 (4H, m, Ar-H), 7.74 (1H, s, Ar-H), 7.76 (1H, s, Ar-H).

4) 5A: reddish purple needles of mp 141-142°C (dec.) (from n-hexane). HR-EIMS: 520.2363 (Calcd 520.2362 for C\(_{33}\)H\(_{32}\)N\(_2\)O\(_4\)). UV \(\lambda_{\text{max}}\) (EtOH) nm (log e): 227 (4.70), 294 (4.45), 469 (3.60). IR (KBr) cm\(^{-1}\): 3352, 1644, 1636, 1226. \(^1\)H-NMR spectrum (CDCl\(_3\)) \(\delta\): 1.84 (6H, s, C(\(\text{CH}_3\))_2\text{CH}=\text{CH}_2\text{)}, 1.85 (6H, s, C(\(\text{CH}_3\))_2\text{CH}=\text{CH}_2\text{)}, 3.86 (3H, s, OCH\(_3\)), 5.26 (1H, d, J=17.6 Hz, C(\(\text{CH}_3\))_2\text{CH}=\text{CH}_2\text{)}, 5.27 (1H, d, J=17.6 Hz, C(\(\text{CH}_3\))_2\text{CH}=\text{CH}_2\text{)}, 5.28 (1H, d, J=10.4 Hz, C(\(\text{CH}_3\))_2\text{CH}=\text{CH}_2\text{)}, 5.29 (1H, d, J=10.4 Hz, C(\(\text{CH}_3\))_2\text{CH}=\text{CH}_2\text{)}, 6.23 (2H, dd, J=10.4, 17.6 Hz, 2C(\(\text{CH}_3\))_2\text{CH}=\text{CH}_2\text{)}, 7.15-7.19 (4H, m, Ar-H), 7.55-7.64 (4H, m, Ar-H), 7.67 (1H, s, Ar-H), 7.68 (1H, s, Ar-H), 7.78 (1H, s, OH).

5) 1B was prepared by reaction of p-xyloquinone and sulfanilic acid in 0.15 N HCl.\(^8\)

6) 3B: yellow needles of mp 137-139°C (from n-hexane). HR-EIMS: 210.0532 (Calcd 210.0528 for C\(_{10}\)H\(_{10}\)O\(_5\)). UV \(\lambda_{\text{max}}\) (EtOH) nm (log e): 271 (4.18), 417 (2.87). IR (KBr) cm\(^{-1}\): 3400, 1768, 1670, 1648, 1294, 1200. \(^1\)H-NMR spectrum (CDCl\(_3\)) \(\delta\): 1.95 (3H, s, CH\(_3\)), 1.97 (3H, s, CH\(_3\)), 2.36 (3H, s, OCOCH\(_3\)), 7.00 (1H, s, OH). 4B: yellow prisms of mp 48°C (from petr.ether). HR-EIMS: 224.0660 (Calcd 224.0685 for C\(_{11}\)H\(_{12}\)O\(_5\)). UV \(\lambda_{\text{max}}\) (EtOH) nm (log e): 268 (4.13), 378 (2.79). IR (KBr) cm\(^{-1}\): 1766, 1676, 1654, 1622, 1274, 1188. \(^1\)H-NMR spectrum (CDCl\(_3\)) \(\delta\): 1.93 (3H, s, CH\(_3\)), 1.95 (3H, s, CH\(_3\)), 2.35 (3H, s, OCOCH\(_3\)), 4.02 (3H, s, OCH\(_3\)). 5B: red needles of mp 119-117°C (dec.) (from n-hexane) (ref.\(^9\)) 165-180°C. HR-EIMS: 182.0579 (Calcd 182.0579 for C\(_9\)H\(_{10}\)O\(_4\)). UV \(\lambda_{\text{max}}\) (EtOH) nm (log e): 286 (4.19), 412 (2.53). IR (KBr) cm\(^{-1}\): 3384, 1646, 1614, 1292. \(^1\)H-NMR spectrum (CDCl\(_3\)) \(\delta\): 1.91 (3H, s, CH\(_3\)), 1.94 (3H, s, CH\(_3\)), 4.09 (3H, s, OCH\(_3\)), 7.11 (1H, s, OH). 6B: orange yellow needles of mp 129-130°C (from EtOH) (ref.\(^10\)) 130-131°C.

7) 3C: yellow needles of mp 113-116°C (dec.) (from n-hexane). HR-EIMS: 182.0208 (Calcd 182.0215 for C\(_9\)H\(_{10}\)O\(_5\)). UV \(\lambda_{\text{max}}\) (EtOH) nm (log e): 264 (4.18), 388 (2.76). IR (KBr) cm\(^{-1}\): 3292, 1792, 1686, 1658, 1622, 1388, 1132. \(^1\)H-NMR spectrum (CDCl\(_3\)) \(\delta\): 2.35 (3H, s, OCOCH\(_3\)), 6.14 (1H, s, Ar-H), 6.63 (1H, s, Ar-H), 7.07 (1H, s, OH). 4C: yellow-orange needles of mp 125-126°C (dec.) (from n-hexane) (ref.\(^11\)) 124°C. HR-EIMS: 196.0368 (Calcd 196.0372 for C\(_9\)H\(_{10}\)O\(_5\)). UV \(\lambda_{\text{max}}\) (EtOH) nm (log e): 262 (4.15), 357 (3.00). IR (KBr) cm\(^{-1}\): 1764, 1692, 1668, 1646, 1600, 1136. \(^1\)H-NMR spectrum (CDCl\(_3\)) \(\delta\): 2.34 (3H, s, OCOCH\(_3\)), 3.84 (3H, s, OCH\(_3\)), 5.96 (1H, s, Ar-H), 6.52 (1H, s, Ar-H). 5C: yellow-orange needles of mp 172-174°C (dec.) (from n-hexane) (ref.\(^11\)) 179°C. HR-EIMS: 154.0266 (Calcd 154.0266 for C\(_7\)H\(_{16}\)O\(_4\)). UV \(\lambda_{\text{max}}\) (EtOH) nm (log e): 281 (4.37), 390 (2.69). IR (KBr) cm\(^{-1}\): 3368, 1664, 1608, 1230. \(^1\)H-NMR spectrum (CDCl\(_3\)) \(\delta\): 3.89 (3H, s, OCH\(_3\)), 5.93 (1H, s, Ar-H), 6.03 (1H, s, Ar-H), 7.36 (1H, s, OH). 6C: yellow prisms of mp 248-249°C (dec.) (from acetone) (ref.\(^12\)) 250-252°C.


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