2-Amino-9*H*-pyrido[2,3-*b*]indole (AαC) Adducts and Thiol Oxidation of Serum Albumin as Potential Biomarkers of Tobacco Smoke

Khyatiben V. Pathak[1], Medjda Bellamri[2], Yi Wang[1], Sophie Langouët[2], and Robert J. Turesky[1]

[1]Masonic Cancer Center and Department of Medicinal Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

[2]UMR Inserm 1085 IRSET, Rennes1 University, UMS 3480 Biosit, F-35043 Rennes, France

Supplemental data

SUPPLEMENTAL FIGURE LEGENDS

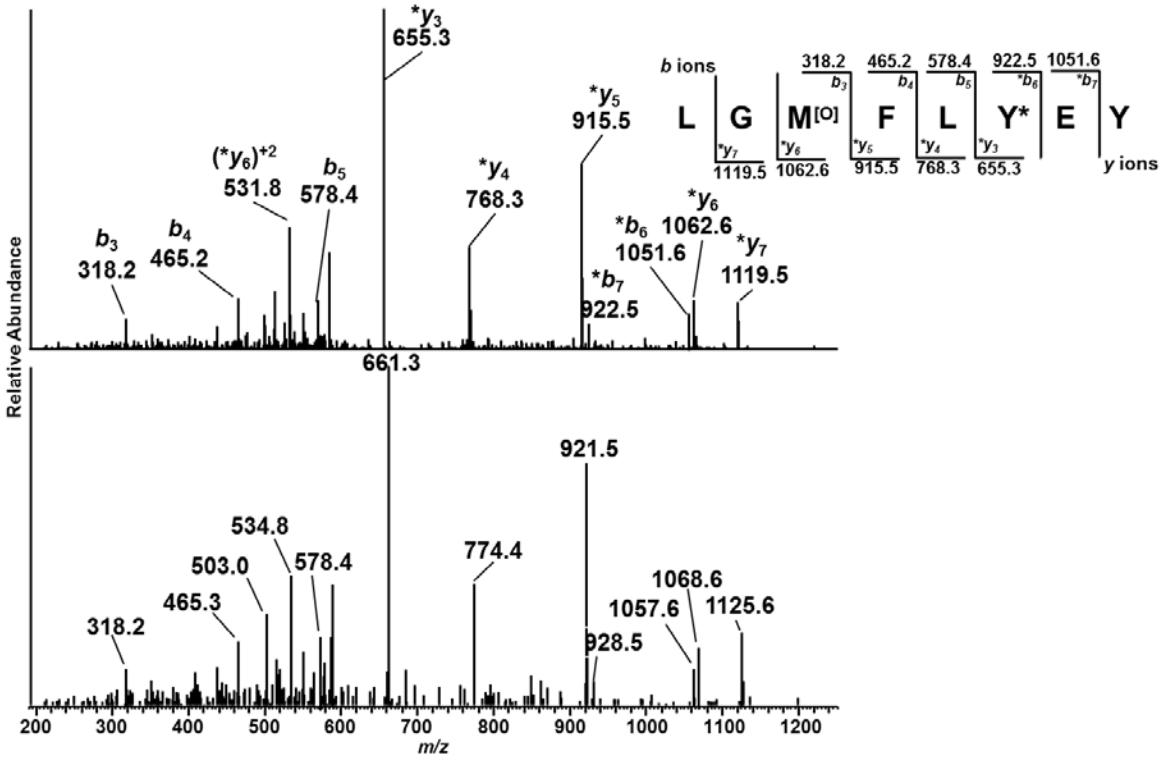
SUPPLEMENTAL FIG. 1S. Product ion spectra of LGMFL*Y$^{[A\alpha C]}$EY adduct (P6) $[M+2H]^{2+}$ at *m/z* 616.5 of SA modified with *N*-acetoxy-AαC (upper panel) and LGMFL*Y$^{[A\alpha C]}$EY adduct (P6) $[M+2H]^{2+}$ at *m/z* *m/z* 619.5 of SA modified with *N*-acetoxy-[$^{13}C_6$]AαC (lower panel), following trypsin-chymotrypsin digestion of SA.

SUPPLEMENTAL FIG. 2S. UPLC-ESI/MS^2 chromatograms AαC-peptide adducts from commercial SA *(A)* and plasma SA (*B*) modified with 1 mole equivalent *N*-acetoxy-AαC following digestion with trypsin/chymotrypsin: LQQ*C$^{[A\alpha C]}$PF sulfenamide ($[M+2H]^{2+}$ at *m/z* 458.7), LQQ*C$^{[SOA\alpha C]}$PF sulfinamide ($[M+2H]^{2+}$ at *m/z* 466.7), LQQ*C$^{[SO_2A\alpha C]}$PF sulfonamide ($[M+2H]^{2+}$ at *m/z* 474.7), LQQ*C$^{[SOA\alpha C]}$PFEDHVK sulfinamide ($[M+3H]^{3+}$ at *m/z* 514.2), LQQ*C$^{[SO_2A\alpha C]}$PFEDHVK sulfonamide ($[M+3H]^{3+}$ at *m/z* 519.6), L*Y$^{[A\alpha C]}$EIAR ($[M+2H]^{2+}$ at *m/z* 473.3), F*Y$^{[A\alpha C]}$PELL ($[M+2H]^{2+}$ at *m/z* 517.3) and full scan spectrum of AαC ($[M+H]^{+}$ at *m/z* 184.1) were used to construct the ion chromatograms.

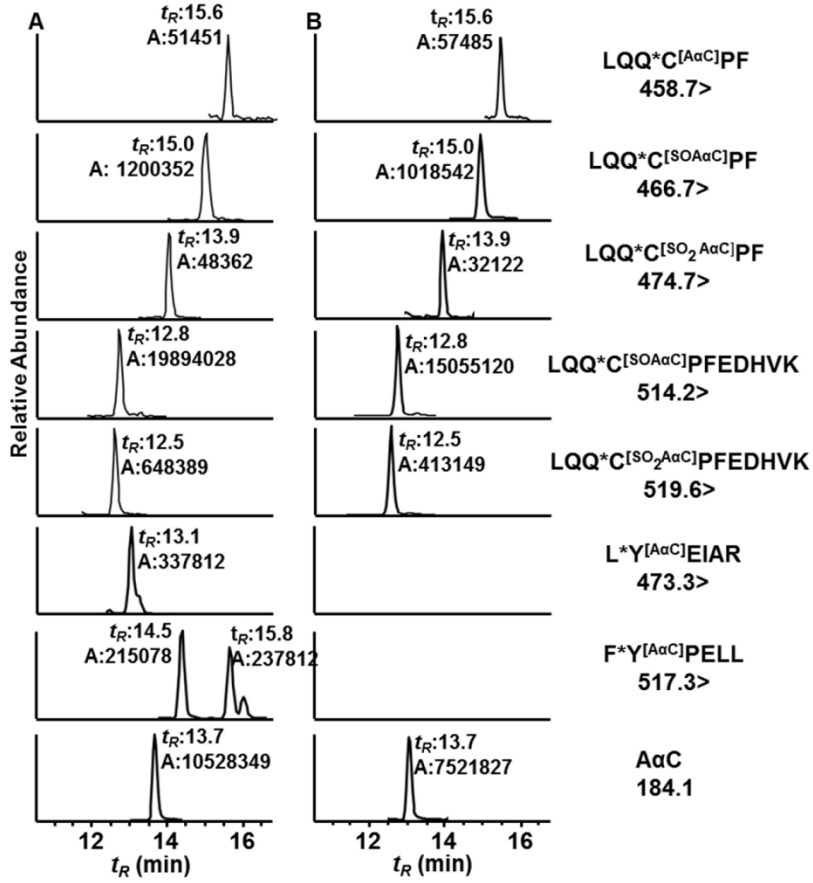
SUPPLEMENTAL FIG. 3S. Product ion spectra of (*A*) LQQ*C$^{[A\alpha C]}$PF sulfenamide ($[M+2H]^{2+}$ at *m/z* 458.7, upper level) and LQQ*C$^{[^{13}C_6A\alpha C]}$PF sulfenamide *m/z* 461.7, lower panel), (*B*) LQQ*C$^{[SOA\alpha C]}$PF sulfinamide ($[M+H]^{+}$ at *m/z* 932.4, upper panel) and LQQ*C$^{[SO^{13}C_6A\alpha C]}$PF sulfinamide ($[M+H]^{+}$ at *m/z* 938.4, lower panel); and (*C*) LQQ*C$^{[SOA\alpha C]}$PFEDHVK sulfinamide ($[M+3H]^{3+}$ at *m/z* 514.2, upper panel) and LQQ*C$^{[SO^{13}C_6A\alpha C]}$PFEDHVK sulfinamide ($[M+3H]^{3+}$ at *m/z* 516.2, lower panel) obtained from trypsin/chymotrypsin digest of SA obtained from human hepatocytes treated with 50 μM of an equimolar mixture of AαC and [$^{13}C_6$]-AαC.

SUPPLEMENTAL FIG. 4S. Product ion spectra of (*A*) LQQ*C$^{[SO_2H]}$PFEDHVK sulfinic acid $[M+2H]^{2+}$ at *m/z* 688.3, (*B*) LQQ*C[SO3H]PFEDHVK sulfonic acid $[M+2H]^{2+}$ at *m/z* 696.3, (*C*) DVFLGM$^{[O]}$F [M+H]+ at *m/z* 844.3 obtained from trypsin/chymotrypsin digest of SA of human hepatocytes treated with 50 μM of an equimolar mixture of AαC and [$^{13}C_6$]AαC.

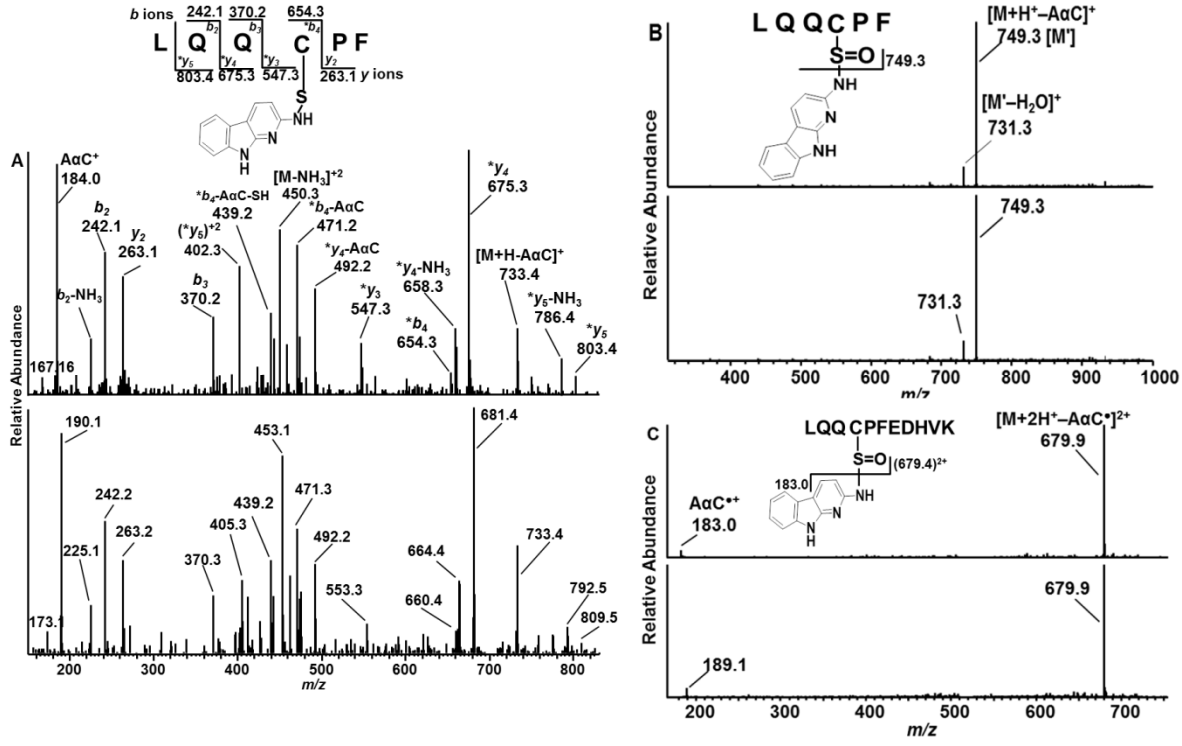
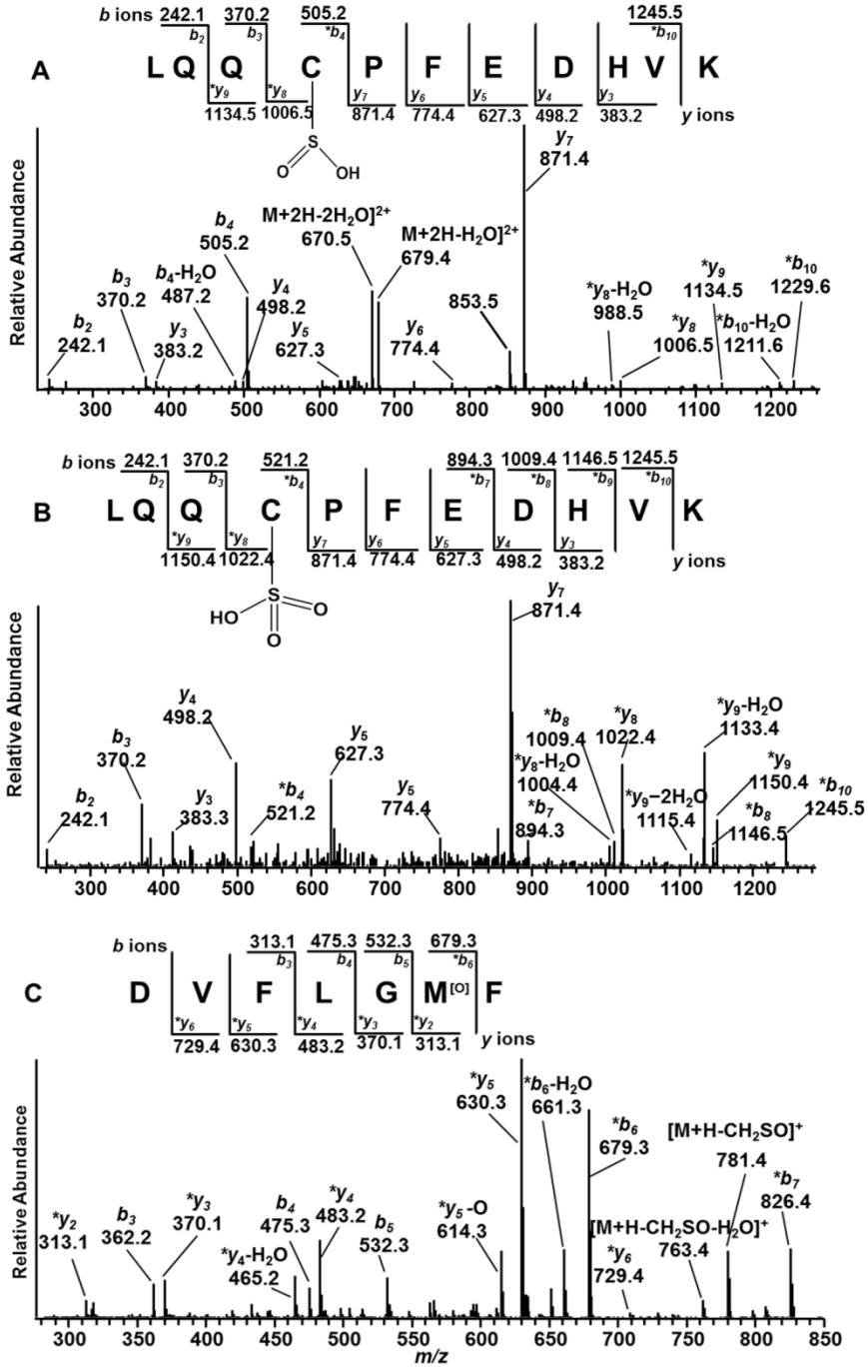
Supplemental Fig. 1S



Supplemental Fig. 2S



Supplemental Fig. 3S



Supplemental Fig. 4S