SUPPLEMENTARY MATERIALS

Table S1. List of hedyotide B2 modification products.

Peptide	Amino Acid Sequence	MW [a]	Observed [b]
B2	IQCGESCVW..IPCISSAW..GCSCKNKICSS	2985	Y
B2a	IQCGESCVW$_{oia}$IPCISSAW..GCSCKNKICSS	3001	Y
B2b	IQCGESCVW..IPCISSAW$_{oia}$GCSCKNKICSS	3001	Y
B2c	IQCGESCVW$_{nfk}$IPCISSAW..GCSCKNKICSS	3017	Y
B2d	IQCGESCVW..IPCISSAW$_{nfk}$GCSCKNKICSS	3017	Y
B2e	IQCGESCVW$_{kyn}$IPCISSAW..GCSCKNKICSS	2989	Y
B2f	IQCGESCVW..IPCISSAW$_{kyn}$GCSCKNKICSS	2989	Y
B2g	IQCGESCVW$_{oia}$IPCISSAW$_{oia}$GCSCKNKICSS	3017	Y
B2h	IQCGESCVW$_{nfk}$IPCISSAW$_{nfk}$GCSCKNKICSS	3049	N
B2i	IQCGESCVW$_{kyn}$IPCISSAW$_{kyn}$GCSCKNKICSS	2993	N
B2j	IQCGESCVW$_{oia}$IPCISSAW$_{nfk}$GCSCKNKICSS	3033	Y
B2k	IQCGESCVW$_{nfk}$IPCISSAW$_{oia}$GCSCKNKICSS	3033	Y
B2l	IQCGESCVW$_{oia}$IPCISSAW$_{kyn}$GCSCKNKICSS	3005	Y
B2m	IQCGESCVW$_{kyn}$IPCISSAW$_{oia}$GCSCKNKICSS	3005	Y
B2n	IQCGESCVW$_{nfk}$IPCISSAW$_{kyn}$GCSCKNKICSS	3021	Y
B2o	IQCGESCVW$_{kyn}$IPCISSAW$_{nfk}$GCSCKNKICSS	3021	Y
B3	QCGESCVW..IPCISSAW..GCSCKNKICSS	2872	Y
B3a	QCGESCVW$_{oia}$IPCISSAW..GCSCKNKICSS	2888	N
B3b	QCGESCVW..IPCISSAW$_{oia}$GCSCKNKICSS	2888	N
B3c	QCGESCVW$_{nfk}$IPCISSAW..GCSCKNKICSS	2904	N
B3d	QCGESCVW..IPCISSAW$_{nfk}$GCSCKNKICSS	2904	N
B3e	QCGESCVW$_{kyn}$IPCISSAW..GCSCKNKICSS	2876	N
B3f	QCGESCVW..IPCISSAW$_{kyn}$GCSCKNKICSS	2876	N
B3g	QCGESCVW$_{oia}$IPCISSAW$_{oia}$GCSCKNKICSS	2904	N
B3h	QCGESCVW$_{nfk}$IPCISSAW$_{nfk}$GCSCKNKICSS	2936	N
B3i	QCGESCVW$_{kyn}$IPCISSAW$_{kyn}$GCSCKNKICSS	2880	N
B3j	QCGESCVW$_{oia}$IPCISSAW$_{nfk}$GCSCKNKICSS	2920	N

B3k	QCGESCVW$_{nfk}$IPCISSAW$_{oia}$GCSCKNKICSS	2920	N
B3l	QCGESCVW$_{oia}$IPCISSAW$_{kyn}$GCSCKNKICSS	2892	N
B3m	QCGESCVW$_{kyn}$IPCISSAW$_{oia}$GCSCKNKICSS	2892	N
B3n	QCGESCVW$_{nfk}$IPCISSAW$_{kyn}$GCSCKNKICSS	2908	N
B3o	QCGESCVW$_{kyn}$IPCISSAW$_{nfk}$GCSCKNKICSS	2908	N
B4	Q*CGESCVW..IPCISSAW..GCSCKNKICSS	2855	Y
B4a	Q*CGESCVW$_{oia}$IPCISSAW..GCSCKNKICSS	2871	N
B4b	Q*CGESCVW..IPCISSAW$_{oia}$GCSCKNKICSS	2871	N
B4c	Q*CGESCVW$_{nfk}$IPCISSAW..GCSCKNKICSS	2887	N
B4d	Q*CGESCVW..IPCISSAW$_{nfk}$GCSCKNKICSS	2887	N
B4e	Q*CGESCVW$_{kyn}$IPCISSAW..GCSCKNKICSS	2859	N
B4f	Q*CGESCVW..IPCISSAW$_{kyn}$GCSCKNKICSS	2859	N
B4g	Q*CGESCVW$_{oia}$IPCISSAW$_{oia}$GCSCKNKICSS	2887	N
B4h	Q*CGESCVW$_{nfk}$IPCISSAW$_{nfk}$GCSCKNKICSS	2919	N
B4i	Q*CGESCVW$_{kyn}$IPCISSAW$_{kyn}$GCSCKNKICSS	2863	N
B4j	Q*CGESCVW$_{oia}$IPCISSAW$_{nfk}$GCSCKNKICSS	2903	N
B4k	Q*CGESCVW$_{nfk}$IPCISSAW$_{oia}$GCSCKNKICSS	2903	N
B4l	Q*CGESCVW$_{oia}$IPCISSAW$_{kyn}$GCSCKNKICSS	2875	N
B4m	Q*CGESCVW$_{kyn}$IPCISSAW$_{oia}$GCSCKNKICSS	2875	N
B4n	Q*CGESCVW$_{nfk}$IPCISSAW$_{kyn}$GCSCKNKICSS	2891	N
B4o	Q*CGESCVW$_{kyn}$IPCISSAW$_{nfk}$GCSCKNKICSS	2891	N

[a] Molecular weights are reported as monoisotopic masses. [b] Observed oxidized derivatives of hedyotide B2. Y is observed and N is not observed under our experimental conditions. Modified tryptophan residues are written in the sequence table as W_{oia}, W_{nfk} and W_{kyn} to denote oxindolylalanine (oia), N-formylkynurenine (nfk) and kynurenine, respectively.

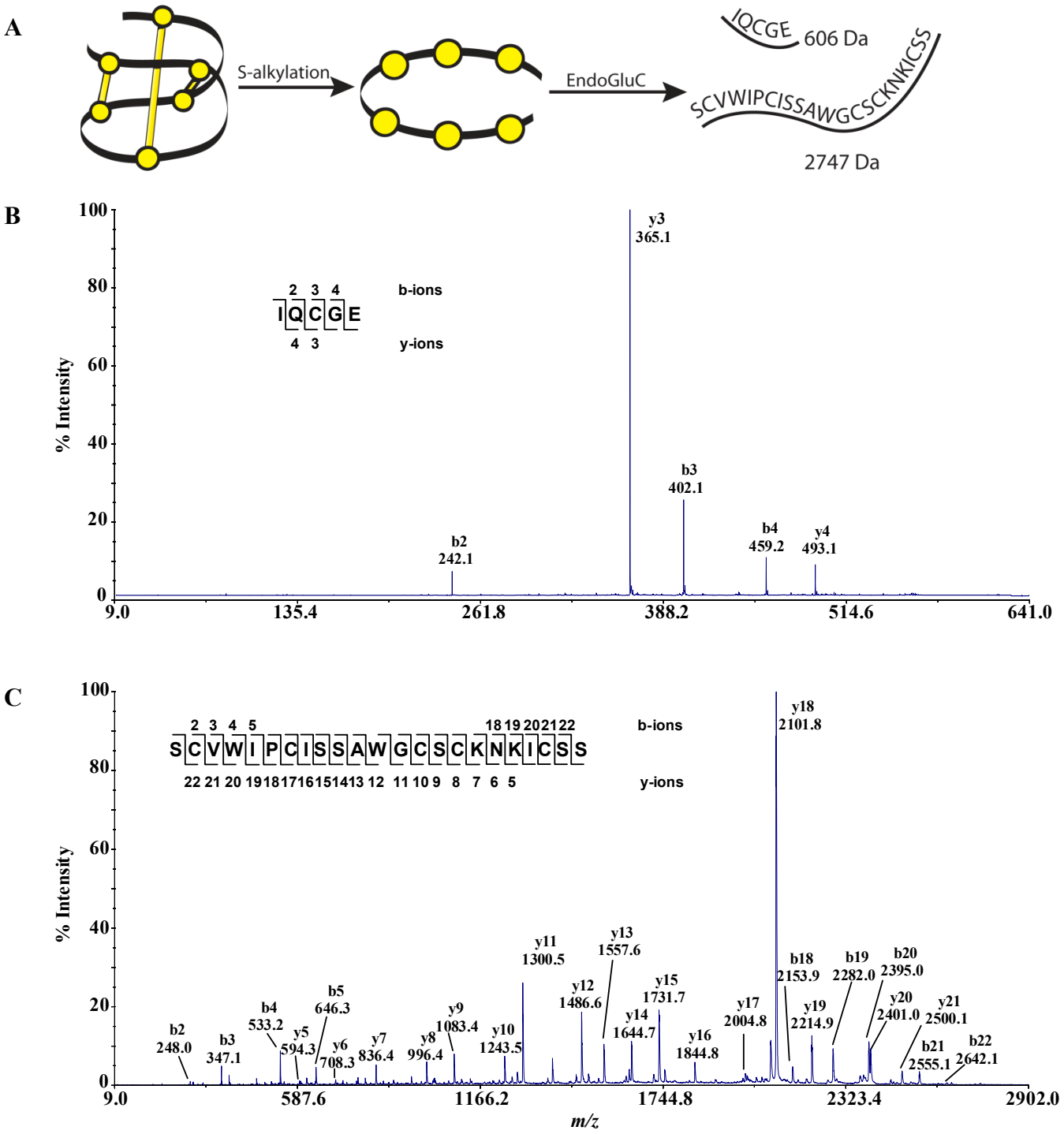

Figure S1. (A) Endoproteinase GluC digestion of S-alkylated hedyotide B2 generated two peptide fragments with *m/z* of 606 and 2747 Da. (B, C) MS/MS spectra of the resulted peptide fragments.