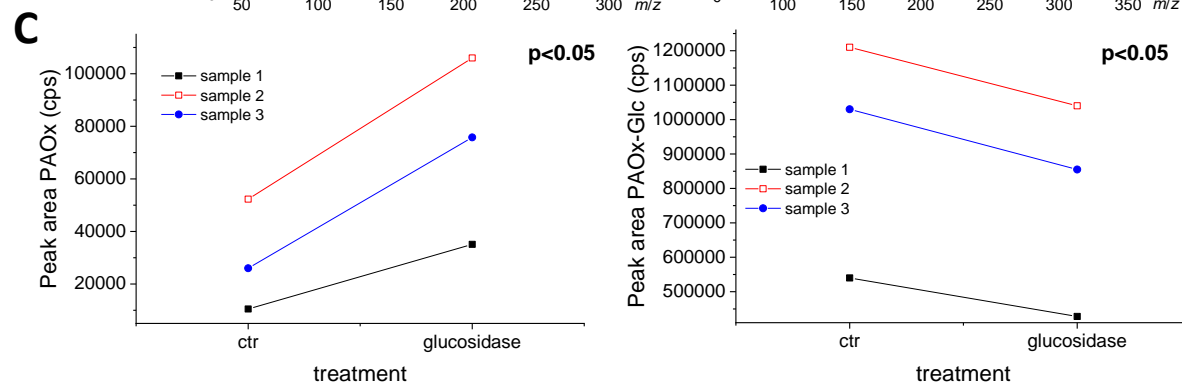
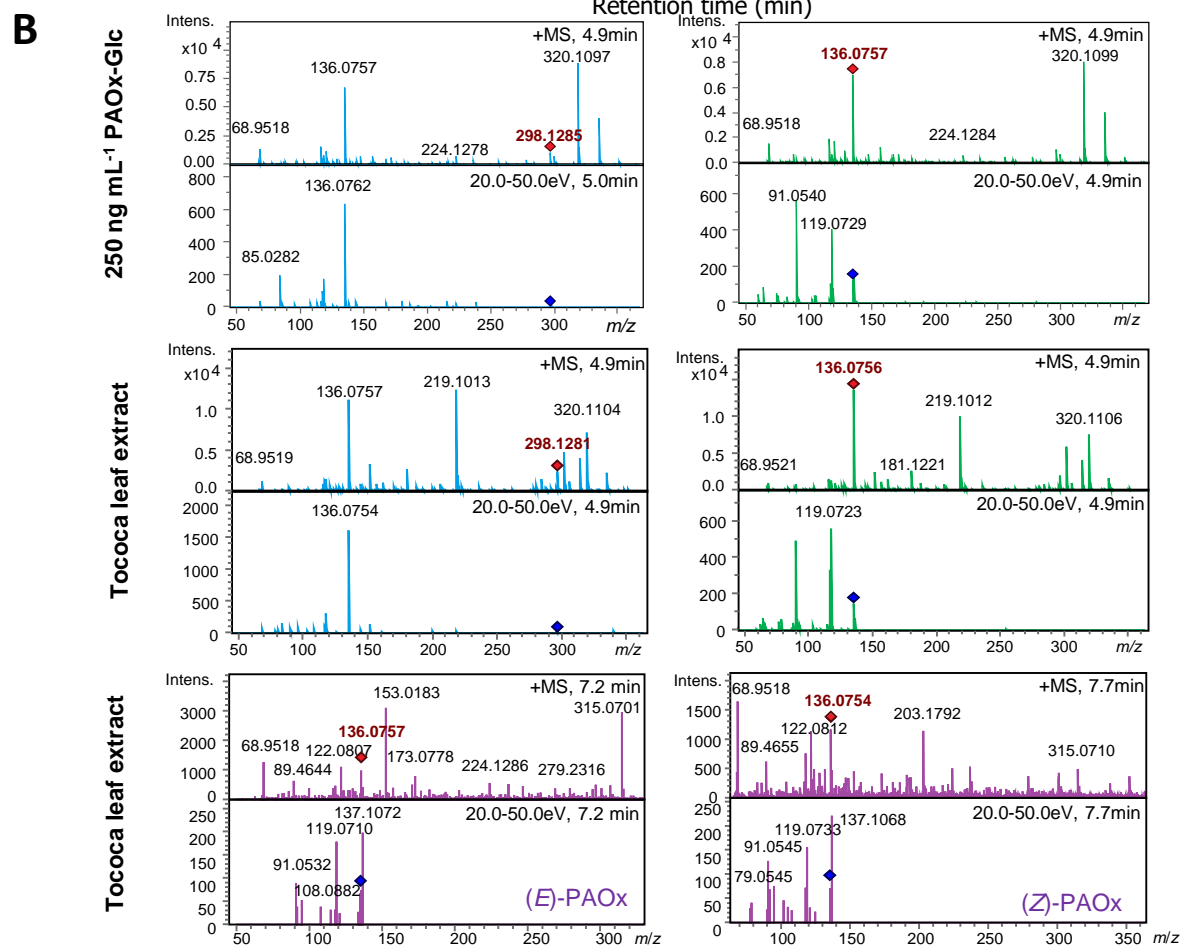
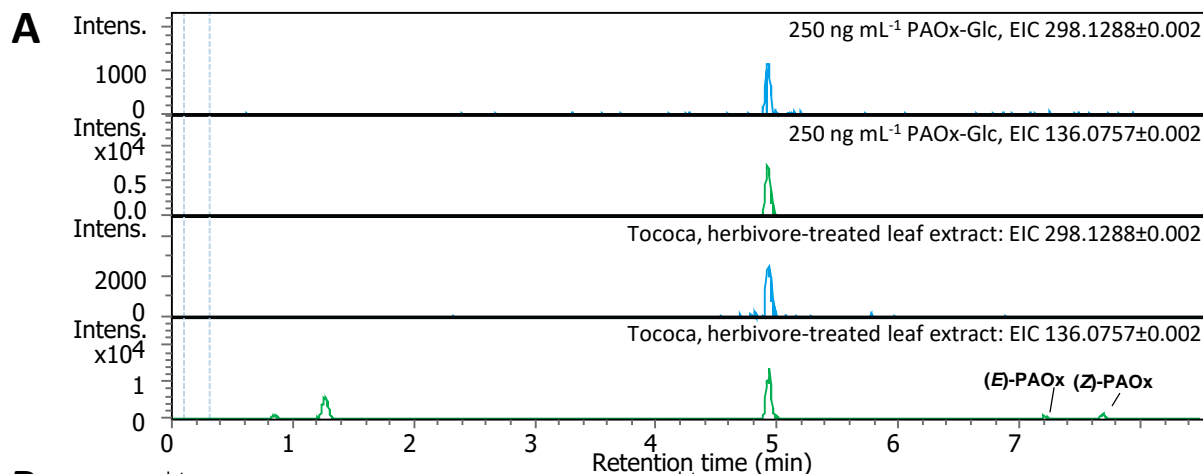
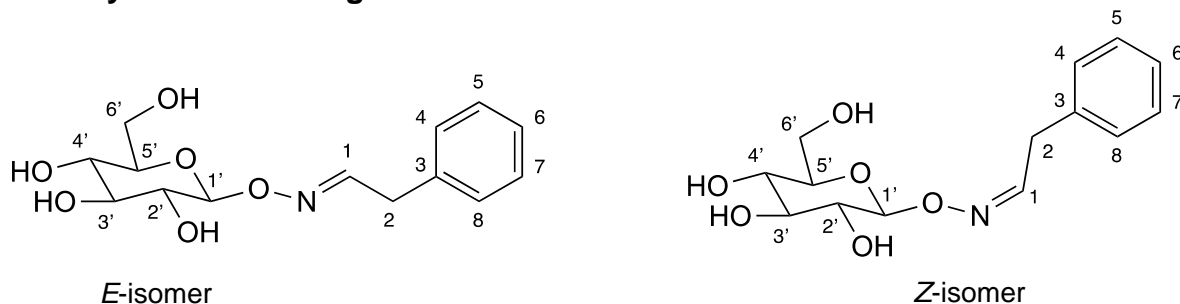


Supplemental Figure S1: Formation of benzyl cyanide in tocooca leaves in response to herbivory (see Figure 1). 3-4 *S. littoralis* caterpillars were allowed to feed on leaves for 24 h and the volatiles were collected simultaneously (light green). Afterwards, the caterpillars were removed from the leaves, put into another bag and their volatiles collected for 24h (blue). Volatiles of the damaged leaves were collected for another 24 h as well (dark green). Samples were analyzed by GC-MS (A) and quantified by GC-FID (B). IS, internal standard; c, contamination; 1, 2-hexenal; 2, 3-hexenol; 3, 1-hexanol; 4, 4-oxo-hex-2-enal and benzaldehyde; 6, 1-octen-3-ol; 7, octan-3-one; 8, benzyl alcohol, 9, β -ocimene; 10, linalool; 12, (*E*)-4,8-dimethyl-nonatriene (DMNT); 14, methyl salicylate; 15, indole; 16, (*E*)- β -caryophyllene; 17, α -farnesene; 18, nerolidol; 19, (*E,E*)-4,8,12-trimethyl-1,3,7,11-tridecatetraene (TMTT); 20, 3-hexenal + hexenal; 21, phenylethyl alcohol; 22, α -humulene; TIC: total ion chromatogram. Means \pm SEM are shown; $n = 5$. Asterisk indicates significant accumulation of benzyl cyanide (> 0) based on one-tailed t-test, $* = p < 0.05$. The absence of volatiles in the blue chromatogram (only caterpillars after feeding on tocooca leaves) indicates that all volatiles detected in the headspace of herbivore-damaged tocooca leaves (dark green) are actually produced by the plant and not by the caterpillars.

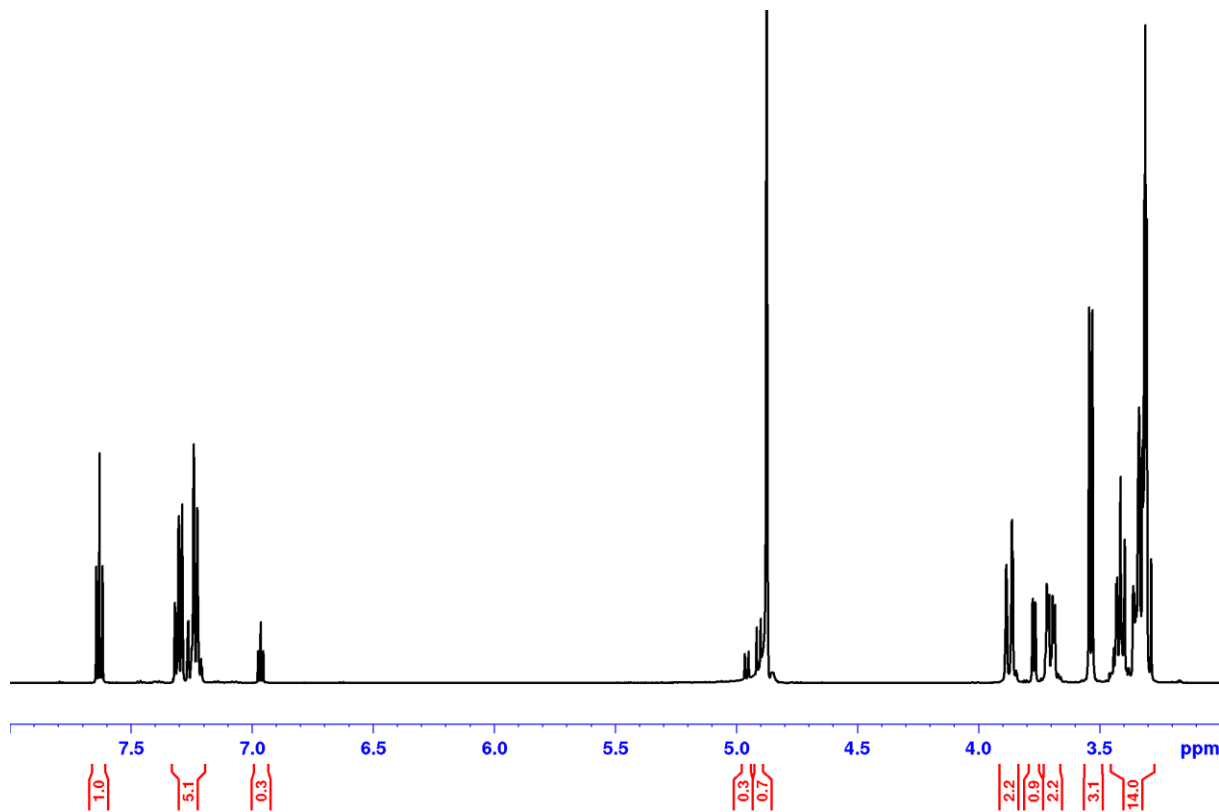


Supplemental Figure S2: Identification of phenylacetaldoxime glucoside (PAOx-Glc) in herbivore-treated tococa leaves. (A) Comparison of retention time and **(B)** fragmentation pattern of synthetic PAOx-Glc and plant-derived PAOx-Glc and PAOx (methanolic extract of *Spodoptera littoralis*-damaged leaves) analyzed by LC-qTOF-MS/MS, the upper mass spectrum is the full scan spectrum, the lower spectra are MS2 spectra after CID of m/z 298.1285 and m/z 136.0757. **(C)** Compounds extracted with 100% methanol from herbivore-damaged leaves were treated with a commercial (Sigma-Aldrich) β -glucosidase from almonds (glucosidase), or only incubated in the reaction buffer (ctr). Paired t-test, $n=3$. cps: counts per second (electron multiplier).

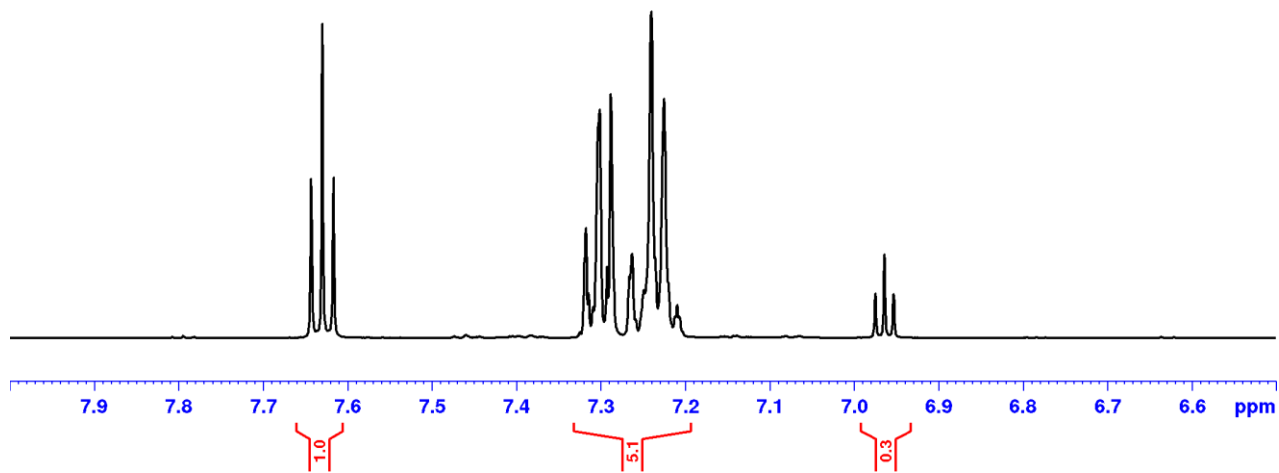
Phenylacetaldoxime glucoside



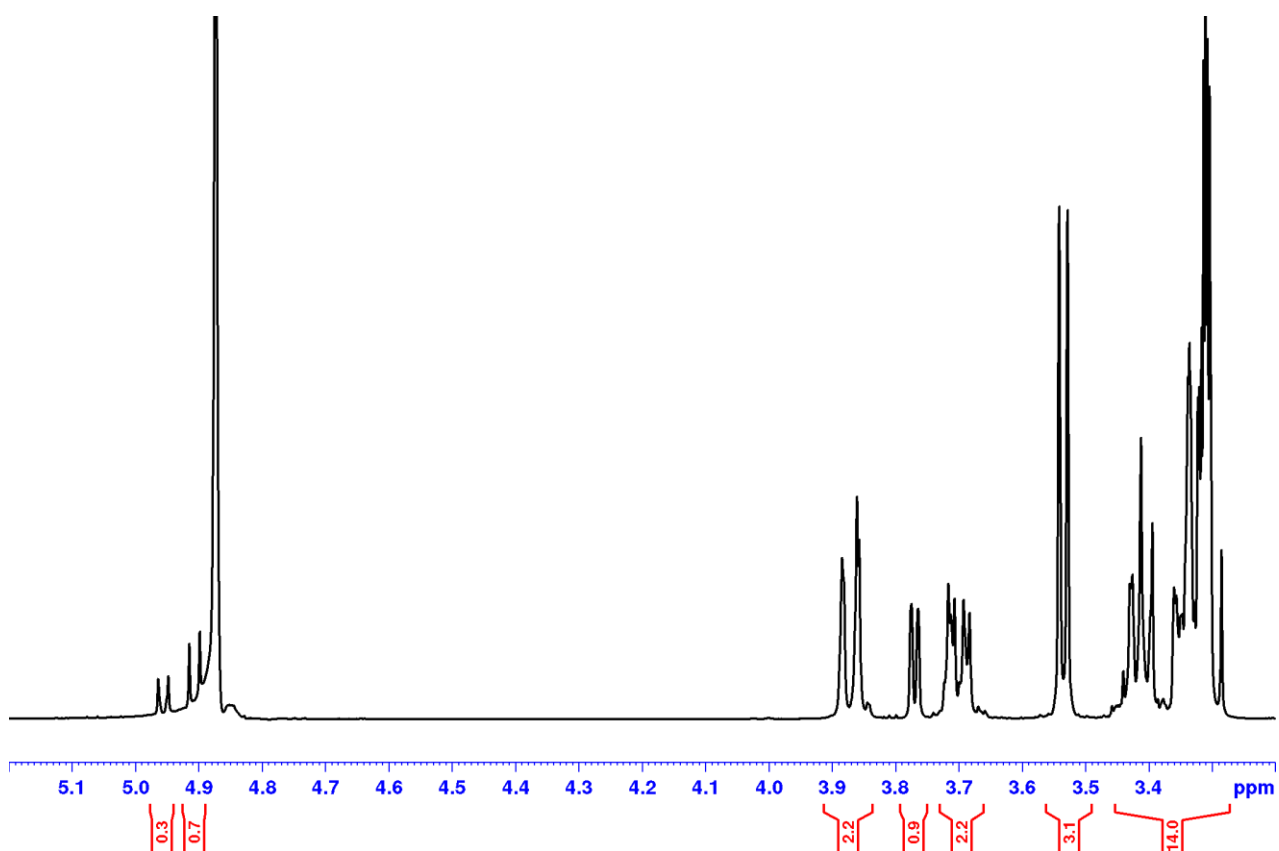
Supplemental Figure S3: The structure of the synthesized phenylacetaldoxime glucoside. $^1\text{H-NMR}$ (500 MHz, $\text{MeOH-}d_3$) for the *E*-isomer: δ ppm: 7.63 (*dd*, $J = 6.7/6.7$ Hz 1H, H-1), 7.30 (*m*, 2H, H-5, H-7), 7.20-7.27 (*m*, 3H, H-4, H-6, H-8), 4.91 (*d*, $J = 8.2$ Hz, 1H, H-1'), 3.87 (*m*, 1H, H-6'), 3.70 (*m*, 1H, H-6'), 3.54 (*d*, $J = 6.7$ Hz, 2H, H-2), 3.30-3.44 (*m*, 4H, H-2', H-3', H-4', H-5'). For the *Z*-isomer (only non-overlapped signals are shown): 6.98 (*dd*, $J = 5.4/5.4$ Hz 1H, H-1), 4.96 (*d*, $J = 8.0$ Hz, 1H, H-1'), 3.77 (*d*, $J = 5.4$ Hz, 2H, H-2). $^{13}\text{C-NMR}$ (125 MHz, $\text{MeOH-}d_3$) *E*-isomer: δ ppm: 153.6 (C-1), 137.2 (C-3), 129.74 (C-4), 129.74 (C-8), 129.67 (C-5), 129.67 (C-7), 127.8 (C-6), 105.6 (C-1'), 78.3 (C-3'), 78.1 (C-5'), 73.56 (C-2'), 71.28 (C-4'), 62.56 (C-6'), 36.5 (C-2). *Z*-isomer: δ ppm: 153.9 (C-1), 137.8 (C-3), 129.8 (C-4), 129.8 (C-8), 129.67 (C-5), 129.67 (C-7), 127.6 (C-6), 105.7 (C-1'), 78.4 (C-3'), 78.1 (C-5'), 73.59 (C-2'), 71.3 (C-4'), 62.63 (C-6'), 33.4 (C-2). *E/Z*-configurations were assigned based on chemical shifts of the oxime protons (Karabatsos & Hsi, 1967).



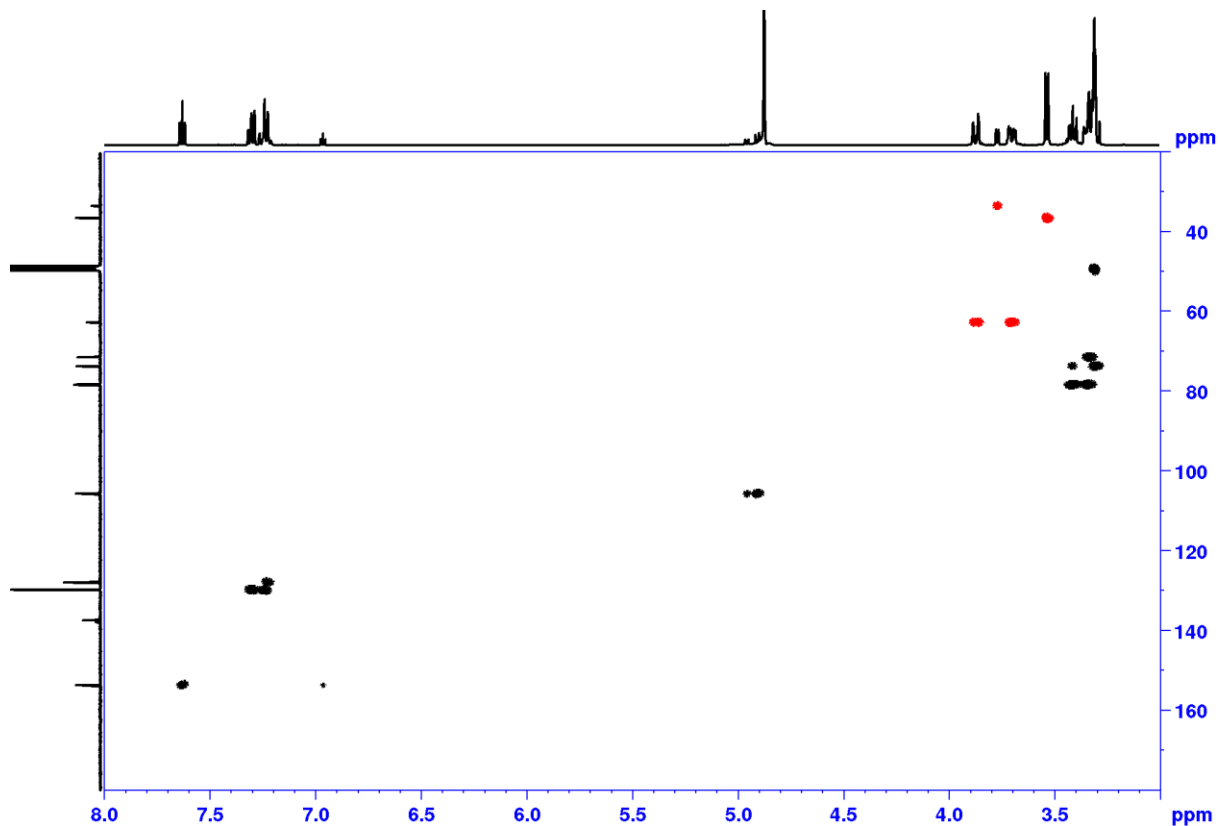
Supplemental Figure S4: Phenylacetaldoxime glucoside, $^1\text{H-NMR}$ with water suppression, full range in $\text{MeOH-}d_3$



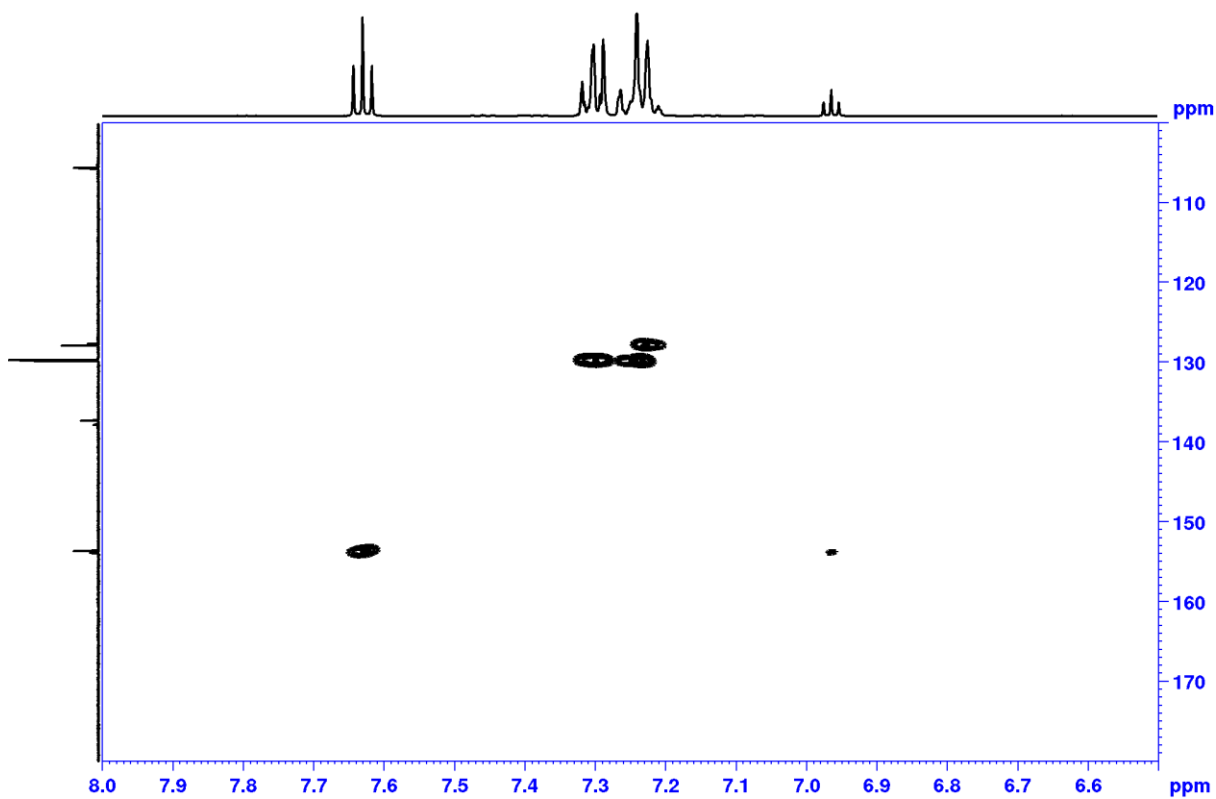
Supplemental Figure S5: Phenylacetaldoxime glucoside, ^1H NMR with water suppression, aromatic range in $\text{MeOH-}d_3$



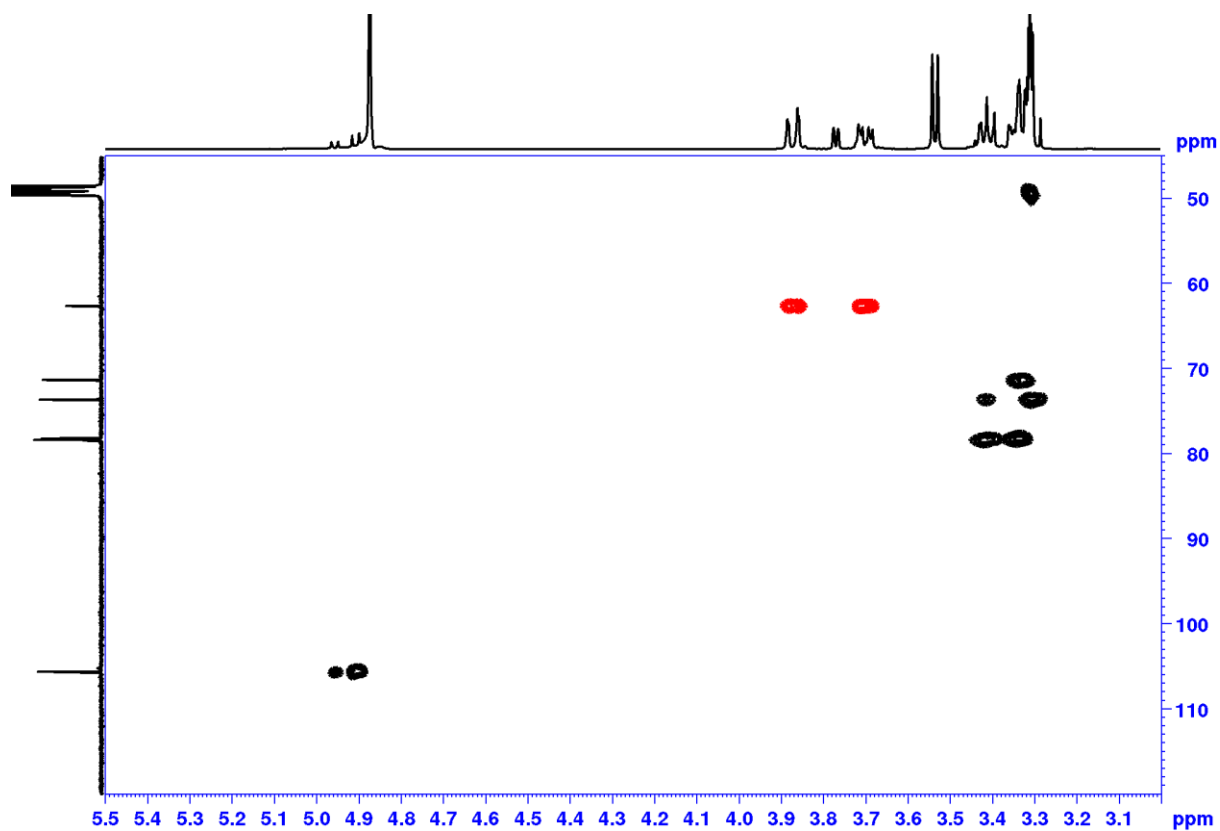
Supplemental Figure S6: Phenylacetaldoxime glucoside, ^1H NMR with water suppression, aliphatic range in $\text{MeOH-}d_3$



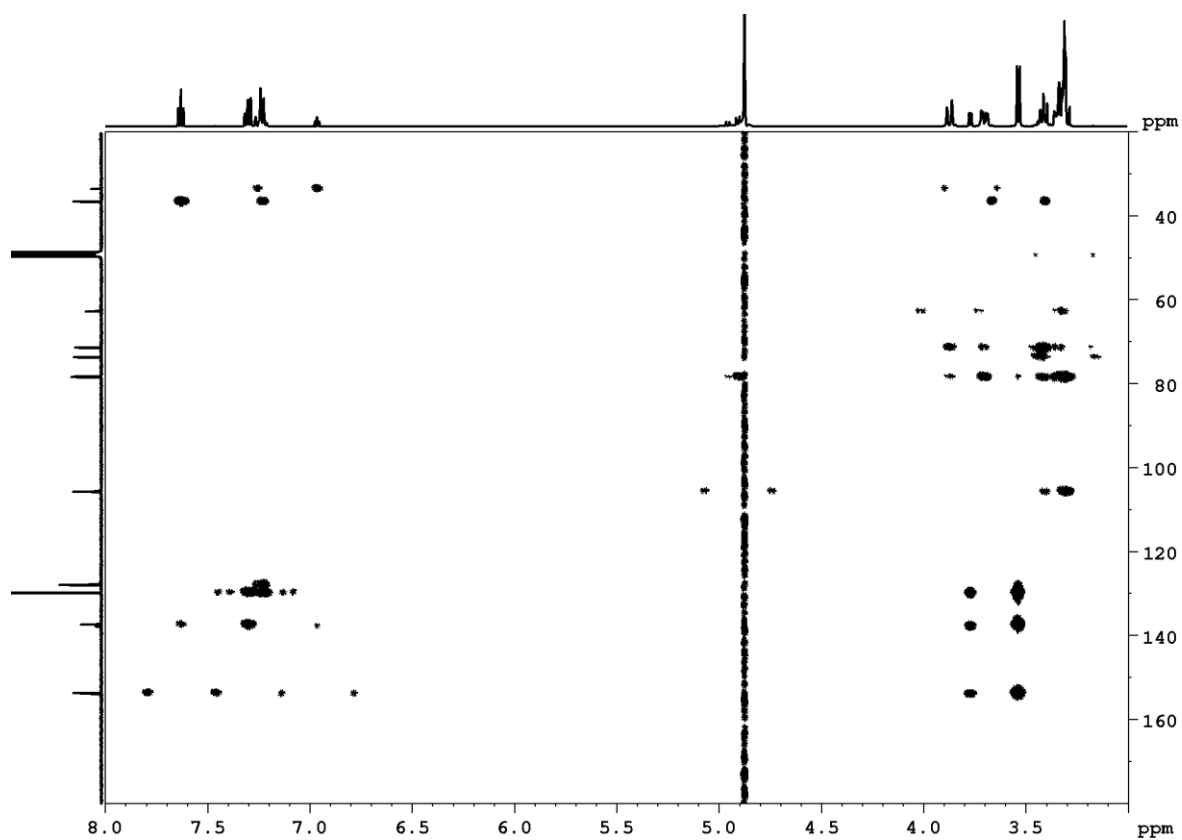
Supplemental Figure S7: Phenylacetaldoxime glucoside, phase sensitive HSQC, full range in MeOH- d_3



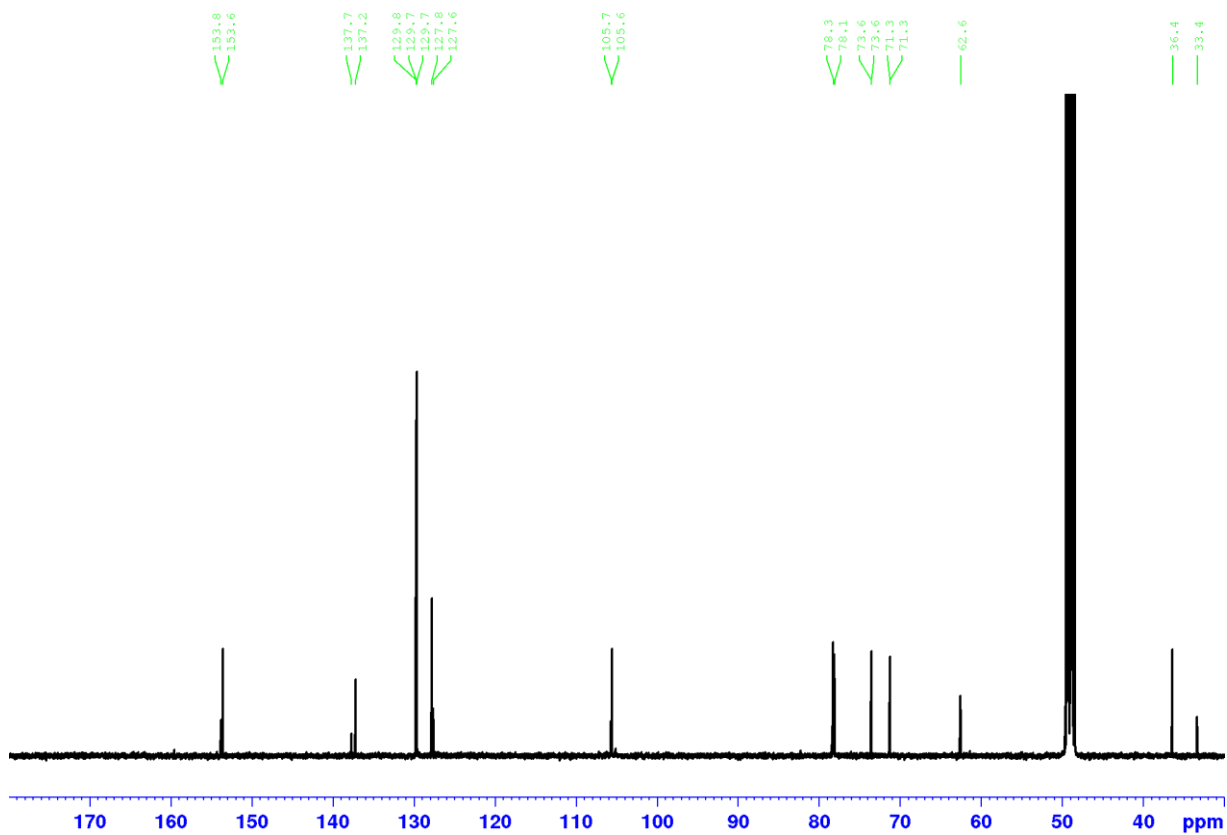
Supplemental Figure S8: Phenylacetaldoxime glucoside, phase sensitive HSQC, aromatic range in MeOH- d_3



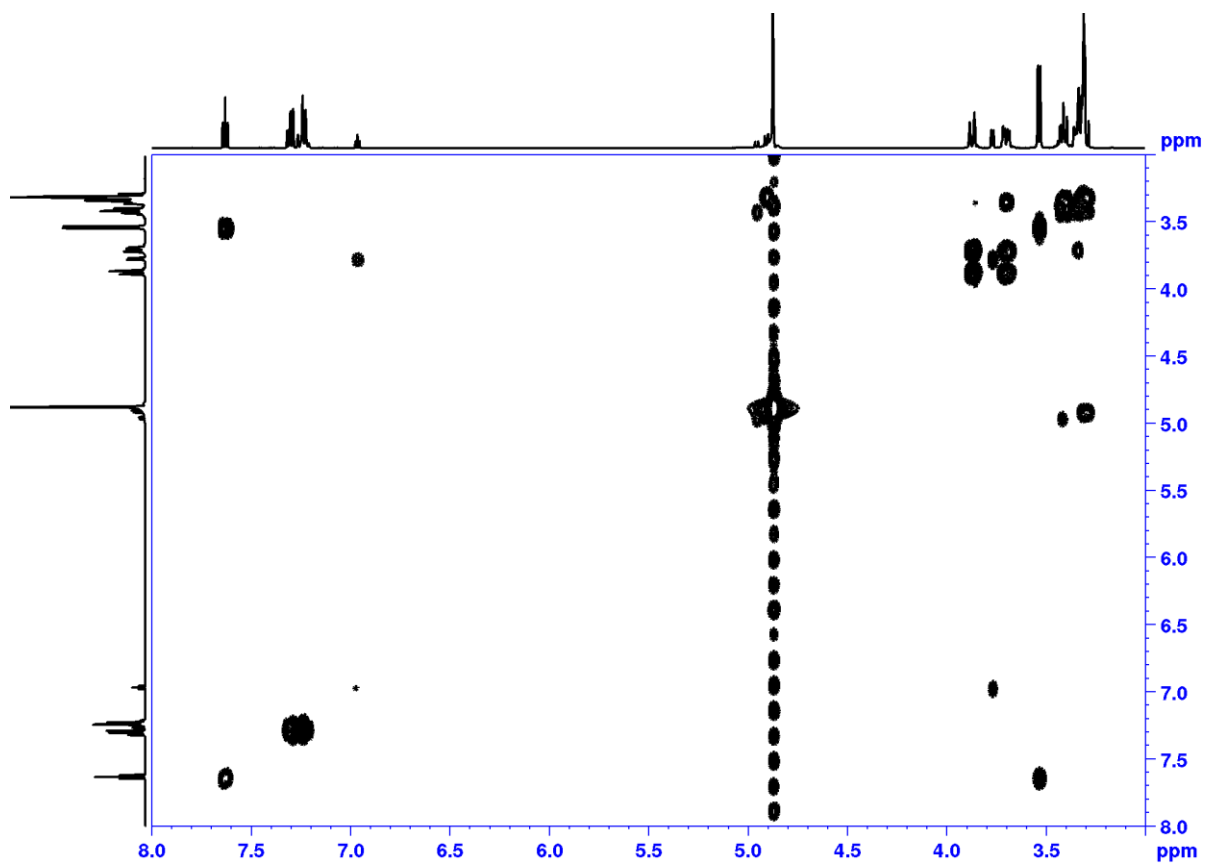
Supplemental Figure S9: Phenylacetaldoxime glucoside, phase sensitive HSQC, aliphatic range in MeOH- d_3 . Shaded areas mark impurity and solvent, red: CH₂, black: CH, CH₃



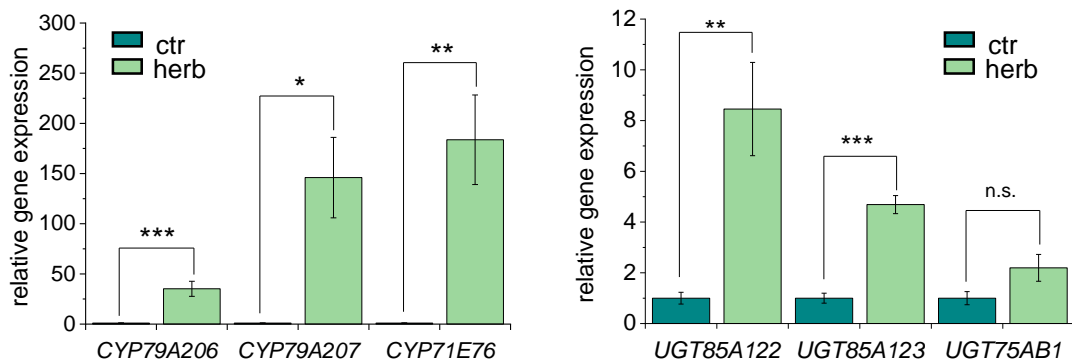
Supplemental Figure S10: Phenylacetaldoxime glucoside, HMBC, full range in MeOH- d_3



Supplemental Figure S11: Phenylacetaldoxime glucoside, ^{13}C , full range in $\text{MeOH-}d_3$



Supplemental Figure S12: Phenylacetaldoxime glucoside, $^1\text{H-}^1\text{H}$ DQF COSY with water suppression. Magnitude mode processed, aliphatic range in $\text{MeOH-}d_3$

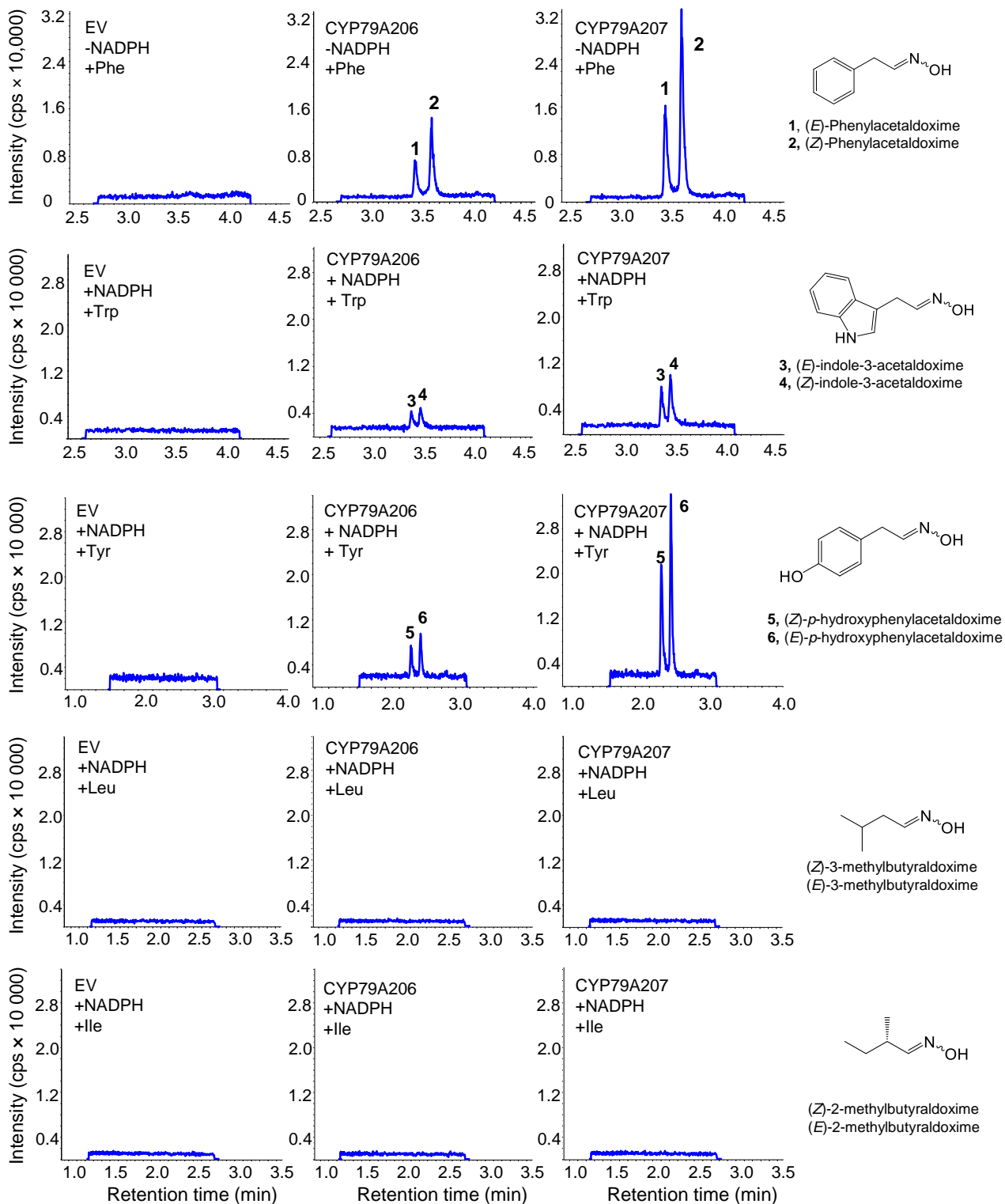


Supplemental Figure S13: Quantitative reverse transcription PCR (RT-qPCR) of PAOx-Glc and benzyl cyanide biosynthesis genes. Expression was analyzed in *Spodoptera littoralis*-damaged and undamaged tococha leaves. The RNA of the treated leaves was isolated, transcribed to cDNA, and RT-qPCRs performed using the primers mentioned in Supplemental Table S12 and actin as housekeeping gene. Relative expression was calculated with the $\Delta\Delta$ Ct method (Pfaffl, 2001). Data are presented as mean \pm SEM; Student's t-test: n = 5 - 7, * = p<0.05, ** = p<0.01, *** = p<0.001.

Methodology: cDNA synthesis from 800 ng RNA was performed with the RevertAid First Strand cDNA Synthesis Kit (Thermo Scientific) using oligo (dT)₁₈ primers according to the manufacturer's instructions. The obtained cDNA was diluted 1:8 with ddH₂O. Primer pairs were designed to amplify the respective gene (Supplemental Table S12), and their specificity confirmed by agarose gel electrophoresis, melting curve, and standard curve analysis. Samples were run in an optical 96-well plate on the CFX96 Touch™ Real-Time PCR System (Bio-Rad) with the Brilliant III Ultra-Fast SYBR Green QPCR Master Mix (Agilent). PCR conditions are given in Supplemental Table S11. All samples were run in duplicates. Normalized fold expression was calculated with the $\Delta\Delta$ CP method (Pfaffl, 2001). As internal calibrator, cDNA from all samples was pooled and run on each plate.

												PP
TqCYP79A206	MNISASAAIL	PNTSSLNATT	VFTTTPSFLA	ASPLSAFNAF	LVSTFVLLYA	ILKSQQSSQK	SS-----	KQLG--RRPP	70			
TqCYP79A207	MNISAYAAIL	PNTSSLIATT	VIKTKLSFLA	ASPLSAFNAF	VVSTFVLLYA	VLSKQSSSRK	IS-----	KQLG--RRPP	70			
SbCYP79A1	-----	MATMEVEAAA	ATVLAAPLIS	SSAILKLLLF	VVTLSTYLARA	LRRPKKSTTK	CSSTTCASPP	AGVGNPPIPP	70			
PtCYP79D6	-----	-----MEYLA	PTSFTLLSF	TASLLVLAII	LFYFIQSHPK	VK-----	---KHP	43				
PtCYP79D7	-----	-----MEYLA	ATSFTLLRE	PTSLLVLAII	LFYFIQSHPK	VK-----	---KHP	43				
EcoCYP79D62	-----	-----MTYLI	LILIMIILVS	FQALNVR--	-----CNDKSN	RH-----	---QLQ	36				
EcCYP79A125	-----	-----MS	SATLATINAL	LLLALVILCS	IVKQQLCRKT	IR-----	KENPLPIPP	44				
xP												
TqCYP79A206	GPTWFVFLGN	LPBMLSNKPV	FRWHRRLMEF	MNTTEIACVRL	GSHVIVSVC	PRIARELHKK	QDVFASRPE	SMAARSFDG	150			
TqCYP79A207	GPWFVFLGN	LPBMLSHKPV	FRWHRRLMEF	MDTEIACLRL	GSHVIVSVC	PRIARELHKK	QDVFASRPE	SMAARSFDG	150			
SbCYP79A1	GFVWFVFLGN	LPBMLLNKPA	FRWHRRLMEF	MGTEIACVRL	GVHVIVSVC	PRIAREVLRK	QDANFASRPE	TFASETFSGG	150			
PtCYP79D6	GPKRWPIVGC	LPBMLRNKPV	YRWHRRLMEF	MNTTEIACIPL	GNVHVIVPVC	PRIARELHKK	QDNTPASRPE	TMITDLISRG	123			
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EcoCYP79D62	GPKRWPIVGC	LPBMLRNKPV	YRWHRRLMEF	MNTTEIACIPL	GNVHVIVPVC	PRIARELHKK	QDNTPASRPE	TMITDLISRG	116			
EcCYP79A125	GPTWFVFLGN	LPBMLRNKPV	FRWHRRLMEF	MNTTEIACIPL	GSHVIVPVC	PRIARELHKK	QDSFASRPE	SMAASRPE	124			
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TqCYP79A207	YKTAVLVPEHG	IQWKKMRRVL	TSEIICPARH	KWLHDKRVVE	ADNLVRYVLA	QCGVS---R	DVNLRTAARH	YSGNLIRNLM	226			
SbCYP79A1	YRNAVLSPEHG	IQWKKMRRVL	TSEIICPSRH	AWLHDKRVTE	ADNLTRYVYN	LATKAAATGDV	AVDVFHVARE	YCGNLVLRML	230			
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PtCYP79D7	YLITALLSPEHG	IQWKNMKVVL	MTHVLSPEKH	QWLYSKRVBE	ADHLVHYVYN	QCKKSVHQGG	VVNLRTAAQH	YCANLIRKML	203			
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SbCYP79A1	FNRVRFGEPEQ	DGGGPMEV	LHMDAVFTSL	GGLYAFQVSD	YLPLRGLDLD	DGHEKIVKBA	NVAVNRLHPT	VIDRRRWK	310			
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PtCYP79D7	FNRVRFGEPEQ	DGGGPIEBE	EYVDALESCL	NHIVAFQVSD	FLPRLRGLDLD	DGHEKIVKBA	HRIINVKYHDE	IIHERVQGWK	283			
EcoCYP79D62	FNRVRFGEPEQ	DGGGPIEBE	EYVDALESCL	NHIVAFQVSD	FLPRLRGLDLD	DGHEKIVKBA	HRIINVKYHDE	IIHERVQGWK	283			
EcCYP79A125	FNRVRFGEPEQ	DGGGPIEBE	QHVDALFNAL	TYLYAFQVSD	YFPLRGLDLD	DGHEKIVKBA	ARTLRLHPT	IISERIKRWR	281			
N P												
TqCYP79A206	K--SGDSNKK	EPODILDVLI	ALKDSDNGRPE	LTSDEIKRAQT	TEIMVAADN	PSNVAEWAMA	EMINPELILQ	KAVEEDDRVV	384			
TqCYP79A207	K--SGDSNKK	EPODILDVLI	ALKDSDNGRPE	LTSDEIKRAQT	TEIMVAADN	PSNVAEWAMA	EMINPELILQ	KAVEEDDRVV	384			
SbCYP79A1	S-----GERQ	EMEDFHLVLI	TLKDACNRP	LTIIEVKAQS	QDTTFAAVDN	PSNVAEWAMA	EMVNPPEVMA	KAVEEDDRVV	385			
PtCYP79D6	D----GAKK	DTEDLDLILI	TLKDRHGNPE	LTKDEIKRAQT	TEIMVAADN	PSNVAEWAMA	EMINPELILE	KAVEEDDRVV	358			
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EcoCYP79D62	N-----GMKD	REBDLDLILI	ALKDDNNGNPE	LTIIEVKAQS	TEITLATVDN	PSNVAEWAMA	EMINPEMMA	KAVEEDDRVV	351			
EcCYP79A125	DDLRSSENEK	EPODILDVLI	MKDKSNGRPE	LAPQEVRAIT	TEIMVAADN	PSNVAEWAMA	EMINPELILH	KAVEEDDRVV	361			
D FxPER												
TqCYP79A206	GKRRLVQESD	IPHLNVKAC	IREAFRLHPT	APFNPHVAM	SDTVAGVEI	PKGSHVLLSR	IGLGRNPKVM	DEPKREPER	464			
TqCYP79A207	GKRRLVQESD	IPHLNVKAC	IREAFRLHPT	APFNPHVAM	SDTVAGVEI	PKGSHVLLSR	IGLGRNPKVM	DEPKREPER	464			
SbCYP79A1	GRERLVQESD	IPKLNKAK	IREAFRLHPT	APFNPHVAL	ADTTVAGTRV	PKGSHVLLSR	IGLGRNPKVM	DEPKREPER	465			
PtCYP79D6	GRERLVQESD	FAHLNVKAC	IREAFRLHPT	APFNPHVAM	ADTTVANVEI	PKGSHVLLSR	IGLGRNPKVM	DEPKREPER	438			
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EcoCYP79D62	GRERLVQESD	FVKLNKAK	IREAFRLHPT	APFNPHVAM	ADTTVANVEI	PKGSHVLLSR	IGLGRNPKVM	DEPKREPER	431			
EcCYP79A125	GRERLVQESD	IGDLNVKAC	IREAFRLHPT	APFNPHVAM	SDTVAGTRV	PKGSHVLLSR	IGLGRNPEVM	DEPKREPER	441			
I K A S												
TqCYP79A206	HUGDGYNMVI	LDEPDLRFIS	FSTGRRGCIA	ASLGTMTVM	LLFRLDQFT	WEKSPQAPGI	DISESEHDLF	LARPINVAE	544			
TqCYP79A207	HUGDGYNMVI	LDEPDLRFIS	FSTGRRGCIA	ASLGTMTVM	LLFRLDQFT	WEKSLQAPGI	DISESEHDLF	LARPINVAE	544			
SbCYP79A1	HUATAASDV	LDEPDLRFIS	FSTGRRGCIA	ASLGTMTVM	LLFRLDQFT	WEKSPQAPGI	DISESEHDLF	LARPINVAE	545			
PtCYP79D6	HUNE-MEKVV	LDEPDLRFIS	FSTGRRGCIA	VSLGTSMTVM	LLFRLDQFT	WSPAPPQSSIT	DLTIAEDSMA	LARPLCALAK	517			
PtCYP79D7	HUNE-MEKVV	LDEPDLRFIS	FSTGRRGCIA	VSLGTSMTVM	LLFRLDQFT	WSPAPPQSSIT	DLTIAEDSMA	LARPLCALAK	517			
EcoCYP79D62	HUNSN-GDDVV	LDEPDLRFIS	FSTGRRGCIA	VNLGTSMTVM	LLFRLDQFT	WSPAPPQSSIT	DLTIAEDSMA	LARPLCALAK	510			
EcCYP79A125	HUMSDQAEV	LDEPDLRFIS	FSTGRRGCIA	AMLGTSMTVM	LLFRLDQFT	WSPAPPQSSIT	DLTIAEDSMA	LARPLCALAK	521			
TqCYP79A206	PRLFVHLVPS	F-----555										
TqCYP79A207	PRLFVHLVPS	F-----555										
SbCYP79A1	PRLFAHLVPS	ISI-----558										
PtCYP79D6	PRLPEQVYPG	Y-----528										
PtCYP79D7	PRLPEQVYPG	Y-----528										
EcoCYP79D62	PRLFAHLVPS	LTSCINHS 528										
EcCYP79A125	PRLFVHLVPS	-----531										

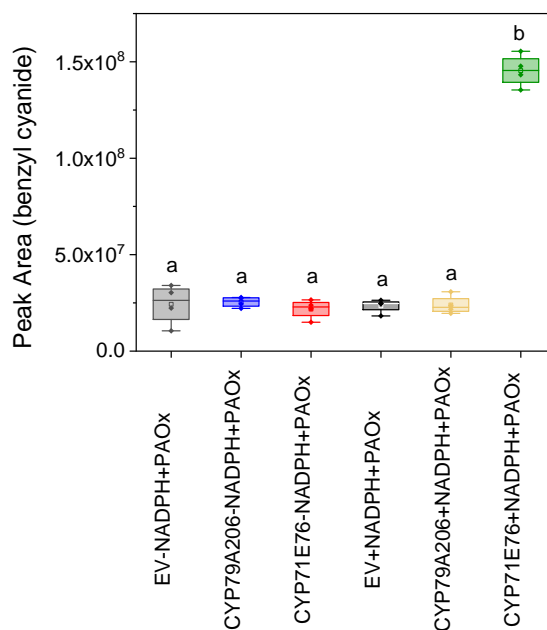
Supplemental Figure S14. Amino acid sequence alignment of CYP79A206 and CYP79A207 with representative CYP79 sequences from other plant species. The alignment was achieved with the ClustalW algorithm using BioEdit. Black shading corresponds to conserved residues, dark grey shades mark residues identical in six of the sequences, and residues with light grey shading are identical in five sequences. Conserved motifs are indicated (see Luck et al, 2016, Bak et al, 2011, Durst et al, 1995).



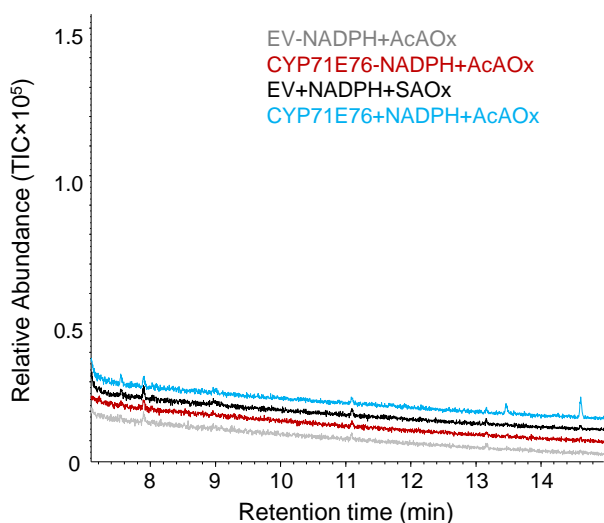
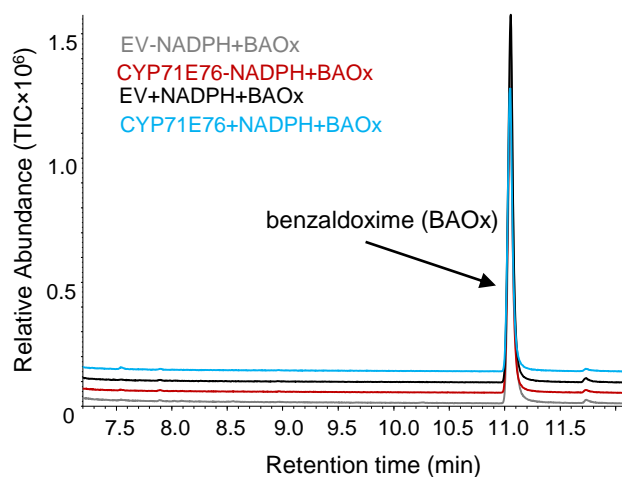
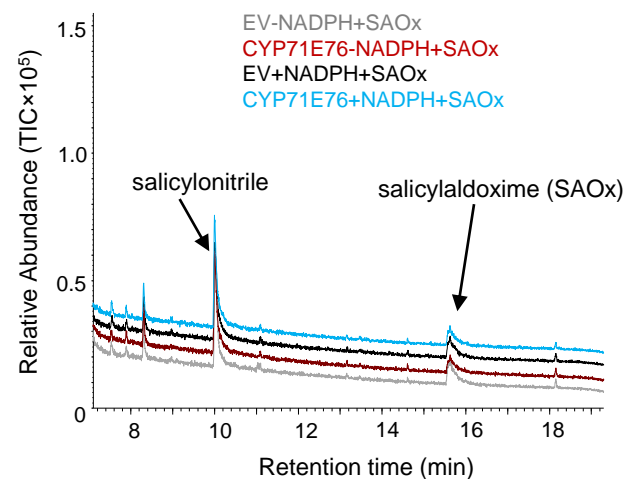
Supplemental Figure S15: Enzymatic activity of CYP79A206 and CYP79A207 with different amino acid substrates. The two genes were heterologously expressed in *Saccharomyces cerevisiae* and microsomes containing the recombinant enzymes were incubated with NADPH and either L-tryptophan (Trp), L-tyrosine (Tyr), L-isoleucine (Ile), or L-leucine (Leu). As negative controls, *S. cerevisiae* was transformed with an empty vector (EV) and the respective microsomes were incubated with the substrates (Phe, Trp, Tyr, Ile, Leu) as well. As a second control, microsomes containing the recombinant enzymes were incubated with Phe in the absence of NADPH. Products were extracted with methanol and detected using LC-MS/MS. cps: counts per second (electron multiplier).

TqCYP71E76	MSSTIIISFP	DN-----F	ILLATFALLI	IPIIFITFLK	R---RNKQQC	DGVR	LA	SP	TF	LI	GNLHQ	LG-K	PHRSI	69						
PtCYP71B40v3	MALYVVPLWL	P-----	LILLLALLL	LFMKKMEVKK	Q-----	SEQLL	PP	SP	KL	PL	GNLHQ	LG-SL	PHQSL	60						
PtCYP71B41v2	MALYVVPLWL	P-----	LILLLALLL	LFMKKMEVKK	Q-----	SEQLL	PP	SP	KL	PL	GNLHQ	LG-SL	PHQSL	60						
FsCYP71AT96	MHLFLQ----		LILLLVIVVI	SLLFLIQKTF	K-----	DVTKQ	FP	FP	RL	PL	GNLHQ	FPSS	CPHLWL	56						
SbCYP71E1	MATTATPQL	GGSV	PQQWQT	CLLVLLPVLL	VSYVLLTSRS	RNRSRS	SGKLG	GAPR	LP	FP	CP	PL	GNLHQ	LG-FL	PHKML	79				
TqCYP71E76	WELSLRKYGFV	MLRL	LDVTVV	LWVSSAEAAK	EVVKTF	VDVT	CSRE	AS	FGTG	RLSY	DL	DLVA	FSPY	PEY	WRE	VKRL	FM	FMM	149	
PtCYP71B40v3	WOLSKKYGFV	MLRL	LDVTVV	LWVSSAEAAK	EVVKTF	VDVT	CSRE	AS	FGTG	RLSY	DL	DLVA	FSPY	PEY	WRE	VKRL	FM	FMM	140	
PtCYP71B41v2	WOLSKKYGFV	MLRL	LDVTVV	LWVSSAEAAK	EVVKTF	VDVT	CSRE	AS	FGTG	RLSY	DL	DLVA	FSPY	PEY	WRE	VKRL	FM	FMM	140	
FsCYP71AT96	HPLSKKYGL	IFLRL	LDVTVV	LWVSSAEAAK	QVVKTF	VDVT	CSRE	AS	FGTG	RLSY	DL	DLVA	FSPY	PEY	WRE	VKRL	FM	FMM	136	
SbCYP71E1	RELARRYGFV	MLRL	LDVTVV	LWVSSAEAAK	EVVKTF	VDVT	CSRE	AS	FGTG	RLSY	DL	DLVA	FSPY	PEY	WRE	VKRL	FM	FMM	159	
TqCYP71E76	SLKRVVHSLWH	IREBEV	DALII	GFLRKNAGN-	-AVEMNERIF	RLTDG	IGTV	AGCN	YGRDK	FGSKS	-FOC	LDE	AMN	MLAR	226					
PtCYP71B40v3	SLKRVVQSFRE	IREBEV	SLLIV	NFISESSALA	APVDLTQKLY	ALVAN	ITFRM	AYCF	NYRGT	DRDK	-EHEM	VHD	TKAV	AGS	219					
PtCYP71B41v2	SLKRVVQSFRE	IREBEV	SLLIV	NFISESSALA	APVDLTQKLY	ALVAN	ITFRM	AYCF	NYRGT	DRDK	-EHEM	VHD	TKAV	AGS	219					
FsCYP71AT96	SSKKVQSFSS	VROBEV	CEMM	KEISRLSGEG	RVVDLSEMM	SITCT	VICRI	AGCK	RYD	GVT	SRCR	WS	ERDL	LKDA	QV	MLAT	216			
SbCYP71E1	SMRRVKAACY	AREBEV	MDRIV	ADLDRAAASK	ASIVINDHVF	RLTDG	IGTV	AGCN	YASKQ	FAHKE	RQHV	LDD	AMDM	MMAS	239					
TqCYP71E76	FSAEHEVFR-R	WGRTI	DRLLG	LTSRLKLIK	DLDYYEYV	EEHKE	SRDN	EQEIG	-DFVD	VLLN	QSD--	PKN	KLAL	TDN	302					
PtCYP71B40v3	ISADEHSIP-Y	LGWIV	DRLLG	HRARTRVVFH	ELDTFFOHL	DNHLKE	GRIK	EHD--	-DMVD	VLLRIE	KEQT	ELGAS	OF	TKD	295					
PtCYP71B41v2	ISADEHSIP-Y	LGWIV	DRLLG	HRARTRVVFH	ELDTFFOHL	DNHLKE	GRIK	EHD--	-DMVD	VLLRIE	KEQT	ELGAS	OF	TKD	295					
FsCYP71AT96	LSFSDYFP--	GMGWIK	KLIG	MSARLDKVFEM	EINNYEET	EEHLN	TIEFM	AKSG	QED	IVD	VLLKL	QRE--	GSLG	FDIT	292					
SbCYP71E1	FSAEHDFENA	AGRLAD	RLSG	FILARRERIN	ELDVF	FEKV	DCHMD	AA	PV	PDNGG	-DFVD	VLLN	LCKE--	HDG	TL	RE	RL	316		
TqCYP71E76	HKKALIMDTI	IGALIS	TSSTI	MLWAMSEIVR	NPRVLKMAQD	EIRNRICK	-K	PR---	VESD	MAKLFY	LRV	V	KET	RL	HPE	378				
PtCYP71B40v3	NKKAIDNLN	MAGVDT	SSST	VNWAMAEIVR	NPRVMKKVQD	EVKRCVGN	-K	GR---	VTESD	IDQLEY	LRV	V	KET	RL	HPE	371				
PtCYP71B41v2	NKKAIDNLN	IGGVD	TSST	VNWAMAEIVR	NPRVMKKVQD	EVKRCVGN	-K	GR---	VTESD	IDQLEY	LRV	V	KET	RL	HPE	371				
FsCYP71AT96	HKKALIMNII	VGATE	TTTAT	VWVVMDELNR	NPEAMKRLQE	ETRF	FMMRKK	TSDMM	IKGED	FEKLVY	LKAV	V	KET	RL	LHEA	372				
SbCYP71E1	HVKAIVLDTI	IGALIS	TSST	ILWAMSEIVR	KQVLRKAQA	EVRAAVG	DDK	PR---	VNSED	AAKIFV	LRV	V	KET	RL	HPE	393				
TqCYP71E76	LALLLPRETI	RPCKIG	GGYDV	PARTRVFNVA	WIGRDRP	ERPE	KDF	PR	FE	-VLER	DFK	GDFEL	LP	PG	SGRR	ICPG	MT	457		
PtCYP71B40v3	GELLPRETI	SHCKV	SCHNI	YPKMLVQINV	WIGRDRP	KDP	EE	FP	PR	FL	-DRS	IDYK	GDFE	YL	PG	SGRR	ICPG	MH	450	
PtCYP71B41v2	ABLLPRETI	SHCKV	SCHNI	YPKMLVQINV	WIGRDRP	KDP	EE	FP	PR	FL	-DSS	IDYK	GDFE	YL	PG	SGRR	ICPG	MH	450	
FsCYP71AT96	ABLLPRETI	GKCVI	EGYEL	QEKTLVFNVA	WIGRDRP	ENPE	EE	FP	PR	FL	-SDK	AV	DFR	GDFE	YL	PG	SGRR	ICPG	IQ	452
SbCYP71E1	ATLLVPRETI	RDTTIC	GGYDV	PANTRVFNVA	WIGRDRP	PAPE	EE	FP	PR	EV	-GSD	V	Y	GSFEL	LP	PG	AGRR	ICPG	LT	472
TqCYP71E76	MGVTTIEFTL	ANLYCY	GDWV	LPFGTKV	EDF	SMEEG	--GI	AIYR	KM	PLRL	VFTK	N----	-	511						
PtCYP71B40v3	MGSITMIEIL	ANLYCF	DWV	FPDGMK	KEDI	NMEBK	AGVSL	ITSK	KT	PLIL	VFVN	LQ---	-	507						
PtCYP71B41v2	MGSITMIEIL	ANLYCF	DWV	FPDGMK	KEDI	NMEBK	AGVSL	ITSK	KT	PLIL	VFVN	LQ---	-	507						
FsCYP71AT96	MGLAMVLAH	VNLIGL	EDWA	LPRGME	EBNL	DLNML	--GI	AVHKE	I	PLRL	IANK	FCC---	-	507						
SbCYP71E1	MGETNVTFTL	ANLYCY	DWA	LPGAMK	EDV	SMEETG	--AA	TFHR	K	PLLV	VFTK	KNRRA	A	531						

Supplemental Figure S16: Amino acid sequence alignment of CYP71E76 with sequences of other nitrile-forming CYP71s and CYP71E1 from *Sorghum bicolor*. The alignment was achieved with the ClustalW algorithm using BioEdit. Black shading corresponds to conserved residues, dark grey shades mark residues identical in four of the sequences, and residues with light grey shading are identical in three of the sequences. Conserved motifs are indicated (Durst and Nelson 1995, Bak et al. 2011)



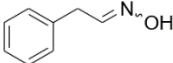
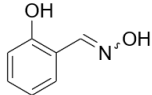
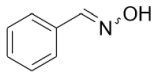
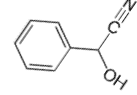
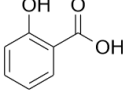
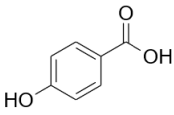
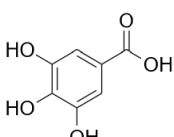
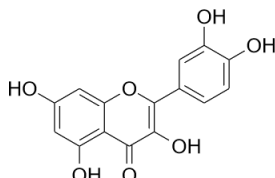
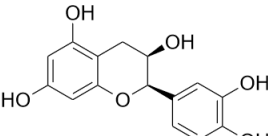
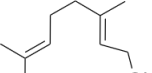
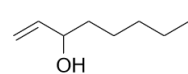
Supplemental Figure S17: Formation of benzyl cyanide by CYP71E76 *in vitro*. Genes were expressed in *S. cerevisiae* and microsomes containing the respective enzymes were used for activity assays with phenylacet-aldoxime (PAOx) as substrate. The hexane phase was analyzed via GC-MS/FID. While benzyl cyanide is always formed from PAOx due to thermal degradation during GC injection, recombinant CYP71E76 in the presence of NADPH was able to generate amounts of benzyl cyanide significantly higher compared to the background. Boxplots (center line, median; box limits, upper and lower quartiles; whiskers, 1.5x interquartile range; open circle, mean). One-Way ANOVA ($F_{5,18} = 238.1$, $p < 0.001$) Tukey HSD *posthoc* test: $p < 0.05$; $n=4$, EV = empty vector.



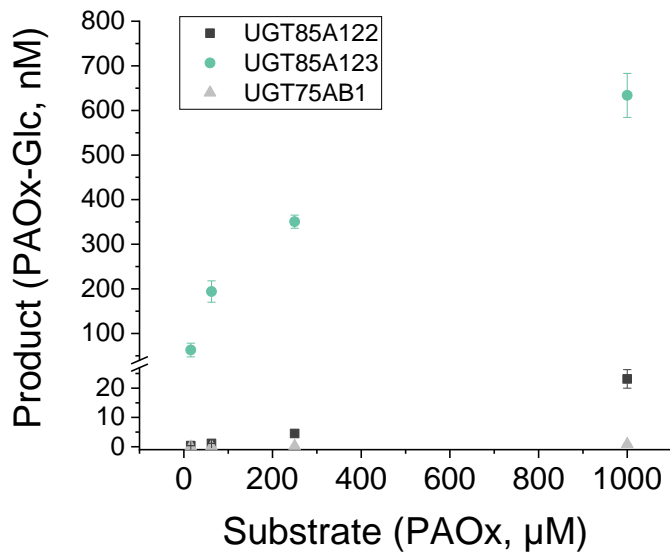
Supplemental Figure S18: CYP71E76 has narrow substrate specificity. The gene was expressed in *S. cerevisiae* and microsomes containing the CYP71E76 were used for activity assays with benzaldoxime (BAOx), salicylaldoxime (SAOx), and acetaldoxime (AcAOx) as potential substrates. The hexane phase was analyzed via GC-MS/FID. Salicylonitrile was always formed from SAOx likely due to thermal degradation during GC injection. The amounts produced in the sample with recombinant CYP71E76 were not higher than the background, indicating no enzyme activity. In addition, no activity was detectable when the microsomes were incubated with BAOx or AcAOx. EV = empty vector.

UGT85A122	--MARDS---	-AVEALPGTK	PHAIIVPYPA	QGHINPELLKL	AKILHGRGCF	HVTFVNTTEYN	ARRLLRSRGP	TSLDDMPG--	72	
UGT85A123	--MSSEQEQS	MKTHVHPNPK	PHAVFIPIPA	QGHINPELLKL	AKLLHRCHGF	HVTFVHTTEYN	HRLLRSRGP	DSLGLGPG--	76	
SbUGT85B1	-----	MGSNAPPPPT	PHVVLVFPFG	QGHVAPLMQL	ARLLHAR-GA	RVTFVYTYQN	YRRLLRKAGE	AAVRPPATSS	69	
UGT75AB1	-----	-----MAP	PHFLLVTFPG	QGHINPSLRF	ARLLIR-IGC	HVTFTTALSA	RRRMSDSKSP	PP-----	54	
AtUGT75B1	-----	-----MAP	PHFLLVTFPA	QGHVNPSSLRF	ARLLIKRTGA	RVTFVTCVSV	FHNSMIANHN	KV-----	55	
UGT76AH1	MGTTSSQDFS	TLNQPNINYN	HKVILFPLPF	QGHMNSMLQL	AQILHSQ-GF	SVTVLHIRYN	PPRPSDHPG-	-----	68	
AtUGT76C1	-----	-----EKRNE	RQVILFPLPL	QGCINAESLQL	AKILYSR-GF	SITLIHTRFN	APKSSDHPL-	-----	53	
UGT85A122	--FHFETIPD	GLPP----VD	ADVMQDVPAL	SDLSLRTCFE	PFVELVSKVN	---QHGG---	PPATCFVYDA	MMPFVADAME	140	
UGT85A123	--FRFETIPD	GLPPTPEDAS	DDVTQDI PSL	CDSTSRTCCTA	PFISLVRRLN	A--EEGG---	PPVSCVVFDD	AMSFALDAAE	149	
SbUGT85B1	ARFRIEVIDD	GLSL-----	SVPQNDVGGL	VDSLRRKNLH	PFRRLLRRLG	Q--EVEGQDA	PPVTCVVGVD	VMTFAAAAAAR	141	
UGT75AB1	EGLSFATFSD	GYDE----GI	KEAELDLVDY	MKEITRRGPE	TLRELILEKR	D-----RG	TNFTHIFFTI	LMPWAADVAO	123	
AtUGT75B1	ENLSPLTFSD	GFDD----GG	ISTYEDRQKR	SVNLKVNQDK	ALSDFIEATK	N-----GD	SPVTCCLYTI	LLNWAQKVAR	124	
UGT76AH1	FDHHPVDVPS	PVAE----L	EAVEGDMTAL	ISLLNWCVV	PFRESLENLM	GESSDGGD--	-HVACLITDI	CWHFTQAIAD	140	
AtUGT76C1	FTF--LQIRD	GLSE-----	QTQSRDLLLQ	LTLNLLNQCQI	PFRECLAKLI	KPSSDSGTED	RKISCVIDDS	GWVFTQSVAE	126	
UGT85A122	KFGLPAVAFW	PPAACAIWGV	AQYPKLIEKG	LVPLKDSYYL	SNG-FLDTVI	EWIPGIDN-F	RLRDIPTFIQ	TTDPNDIMVH	218	
UGT85A123	EFGVPGVAYW	TPSACGVLAY	SYYHKLVEKG	LSPKDKSSYL	TNG-YLDTV	DWIPGMKKN	CLRDLPSFIR	TTDPNDVMVN	228	
SbUGT85B1	EAGIPEVQPF	TASACGLLGY	LHYGELVERG	LVEFRDASLL	ADDDYLDTPL	EWVGMGMH-M	RLRDMPTFCR	TTDPPDVMVS	220	
UGT75AB1	SLGLRSTLVW	IQPATVFYDI	YYHFNGYDQL	IRSSADAAAA	DNG---DSRE	IRLPGMLP-M	TSSYFPSFLA	SGNQYHFSLP	199	
AtUGT75B1	RFQLPSALLW	IQPALVFNIY	YTHFMG---	-----	-----NKS	FELPNLSS-L	EIRDLPSFLT	PSNTNKGAYD	183	
UGT76AH1	ENLSPRMVLR	TTSIGSISAF	SAVSRLQKNG	LLPLPES---	-----QIE	EVIEEVAP-L	RWKDLF--IV	PTR-NPKDF	206	
AtUGT76C1	SFNLRFVFLC	AYKFSFFLGH	FLVPQIRREG	FLVVPDS---	-----EAD	DLVPEFPP-L	RKDLRSLRIMG	TSQ-OSKPLD	194	
UGT85A122	YMIRSVEVSS	KKAC-----	VVFNTFDALF	ADVLRALKSI	YPS-IYTVGP	LNLVLDLDR--	PEEELTAVGS	NLWKEDNSCL	290	
UGT85A123	YVIGEIQRTS	QKSS-----	LVLNTEFKLE	KDVLDAISAI	FPS-VYAIGP	INMLMLDR--	SDELDLSIGS	NLWKEENWCL	300	
SbUGT85B1	ATLQOMESAA	G-SK-----	LILNLTLYEL	KDVVDALAAF	FPP-IYTVGP	LAEVIASSDS	ASAGLAAMD	SIWQEDTRCL	293	
UGT75AB1	YIKRHFEIILN	SEKTTMMPK	VLVNTFEEEL	AEAVKAIDEL	NVIPVGPFPF	LAFLDEQ--H	PTDTSLGGDL	FQKSRDLDYI	277	
AtUGT75B1	AFQEMMEFLI	KET----KPK	ILINTEDSLE	PEALTAFPNI	DMVAVGPLL	TEIFSG---	STNKS-----	--KDQSSSYT	249	
UGT76AH1	RLADIDRAT	KACA-----	LISNSFEELF	EVKLAESRRS	IPIPFLLIGP	FHKRFPS---	-----SSTPVA	GKLLQDQSCI	274	
AtUGT76C1	AYLLKILDAT	KPAS-----	IIVMSCKELD	HDSLAEASNK	FKILYFPIGP	FHIHDV---	-----ASS--S	SLELDPQSCI	260	
UGT85A122	KWLDSQEHGS	VVIYVNFSGSIT	VATAEQMTEF	AWGLANSRME	FLWVIR----	-PDLVVGES-	-AVLPPGFTD	ETS-DRCMS	362	
UGT85A123	HWLDSQDLGS	VVIYVNFSGSIT	VATKEQITEF	AWGLADSKKE	FLWVIR----	-PDLVVGES-	-AVLPPGFTD	ATE-GRGILS	372	
SbUGT85B1	SWLDGKPAQS	VVIYVNFSGSMA	VMTAAQAREF	ALGLASCGSE	FLWVKR----	-PDVVEGEE-	-VLLPEALLD	EVARGRLVW	366	
UGT75AB1	DWLNKQQAAS	VVIYVNFSGSLS	LFSRPQKEEM	AKALIAMGRE	FLWVIR----	---KRMGEE	EEDDKLS-YE	EELSKLGMIV	349	
AtUGT75B1	LWLDSKTESS	VVIYVNFSGTMV	ELSKKQIEEL	ARALIEGKRE	FLWVITDKSN	RETKTEGEE	TEIEKIAGFR	HELEEVGMIV	329	
UGT76AH1	AWLDKQSPKS	TIIYVSEGSIA	SIDERDFLEI	VRGLANSQVE	FLWVVR----	-PGSVRGHW	LVTLPPLLE	---GKCHIV	345	
AtUGT76C1	PWLDMRETRS	VVIYVSLGSLA	SLNESDFLEI	ACGLRNTNQS	FLWVVR----	-PGSVRGHW	IESLPSGFME	SLD-GKCKIV	334	
			PSPG Box			N	G			
UGT85A122	GWCPQEEVLK	HPSIGGFLTH	SGWNSSTLES	SAGVPMVCWF	FFADQOTNCW	YGKNSWGI	GM	EIDHDVKRDK	VEGMVKELME	442
UGT85A123	GWCPQEEVLK	HPSIGGFLTH	CGWNSMMEV	CSGVPVICWF	FFAEQOTNCW	YGKNAWGI	GM	EIDNEVKRDE	VEGMVRELM	452
SbUGT85B1	HWCPQAAVLK	HAAVGLFVSH	CGWNSLLEAT	AAGQPVLAWF	CHGEQOTNCR	QLCEVWNGA	QLPREVESGA	VARLVREMMV	446	
UGT75AB1	HWGSGQEVLS	NPSVGCFFVTH	CGWNSSTESL	VCGVPMVGF	QWSDQOTNAK	LVEEVWRTGV	QVKGNGEGV	VEAGEIERCL	429	
AtUGT75B1	HWGSGQEVLS	HRAVGCFFVTH	CGWNSSTLES	VLGVPVVAWF	MMSDQPTNAK	LLEESWRTGV	RVRE-NKDGL	VERGEIRRCL	408	
UGT76AH1	KWAPQREVLA	HPSVGAFFVTH	NGWNSSTLEA	CEGVPMLSSF	MFGDQVWVAR	HVSDVWRVGI	HLEGLLRDE	IANGIGRLMG	425	
AtUGT76C1	RWAPQDLVLA	HRATGGFLTH	NGWNSSTLES	CEGVPMICLF	KWDQVFNAR	FISEVWRVGI	HLEGRIERRE	IERRVIRLMV	414	
			Consensus sequence							
UGT85A122	GEKG-----	KEMKRAAGW	RSAAEKAVAP	GGSSYKNLEK	LLSLLLPKK-	-----	---	485		
UGT85A123	GEKG-----	KEMKRAAEW	KAAAEAAAP	GGSSHQNEK	LVALLLSEQ-	-----	---	495		
SbUGT85B1	GDLG-----	KEKRAKAAEW	KAAAEAAARK	GGASWRNVER	VVNDLLLVGG	KQ-----	---	492		
UGT75AB1	EVVLGDGEKG	RELRGNAKKW	GELAKKAAKD	GGSSDNNLRR	FVD-----	GL	VKGTASSE--	482		
AtUGT75B1	EAVME--EKS	VELRENAKKW	KRLAMEAGRE	GGSSDKNMEA	FVEDICGESL	IQNLCEAEEV	KVK	469		
UGT76AH1	DSSSS--KER	EMMKRVMDL	KMKVDGCLKP	GGSSYKSLQK	LTCYLFSSCQ	PEKL-----	---	477		
AtUGT76C1	ESKG-----	BEIRGRIKVL	RDEVRRSVKQ	GGSSYRSLDE	LVDRIISIIIE	PLVPT-----	---	463		

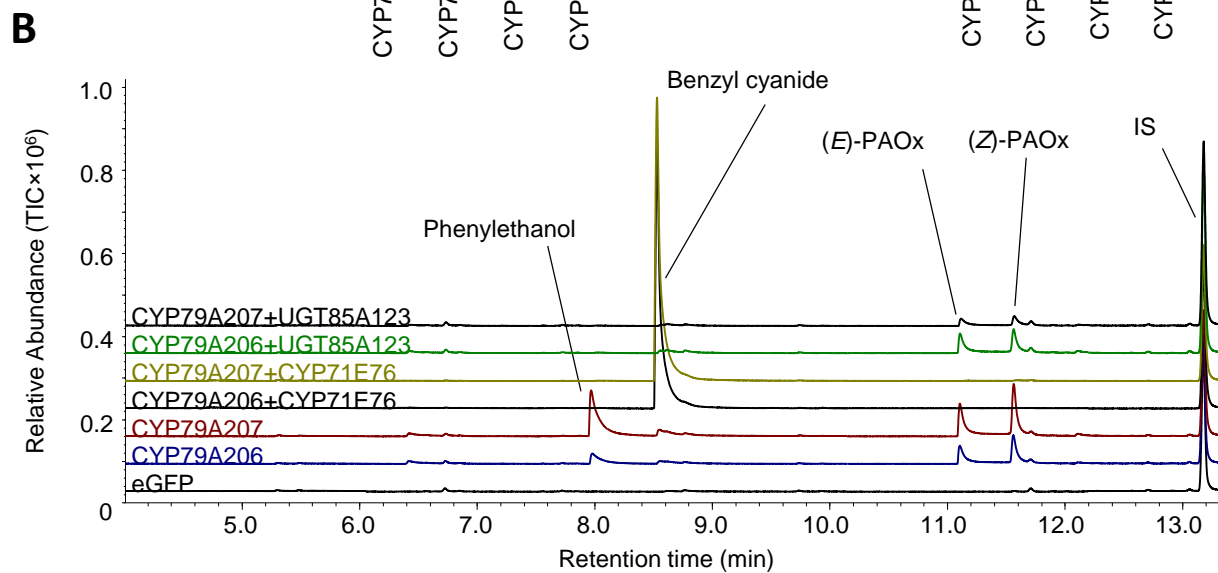
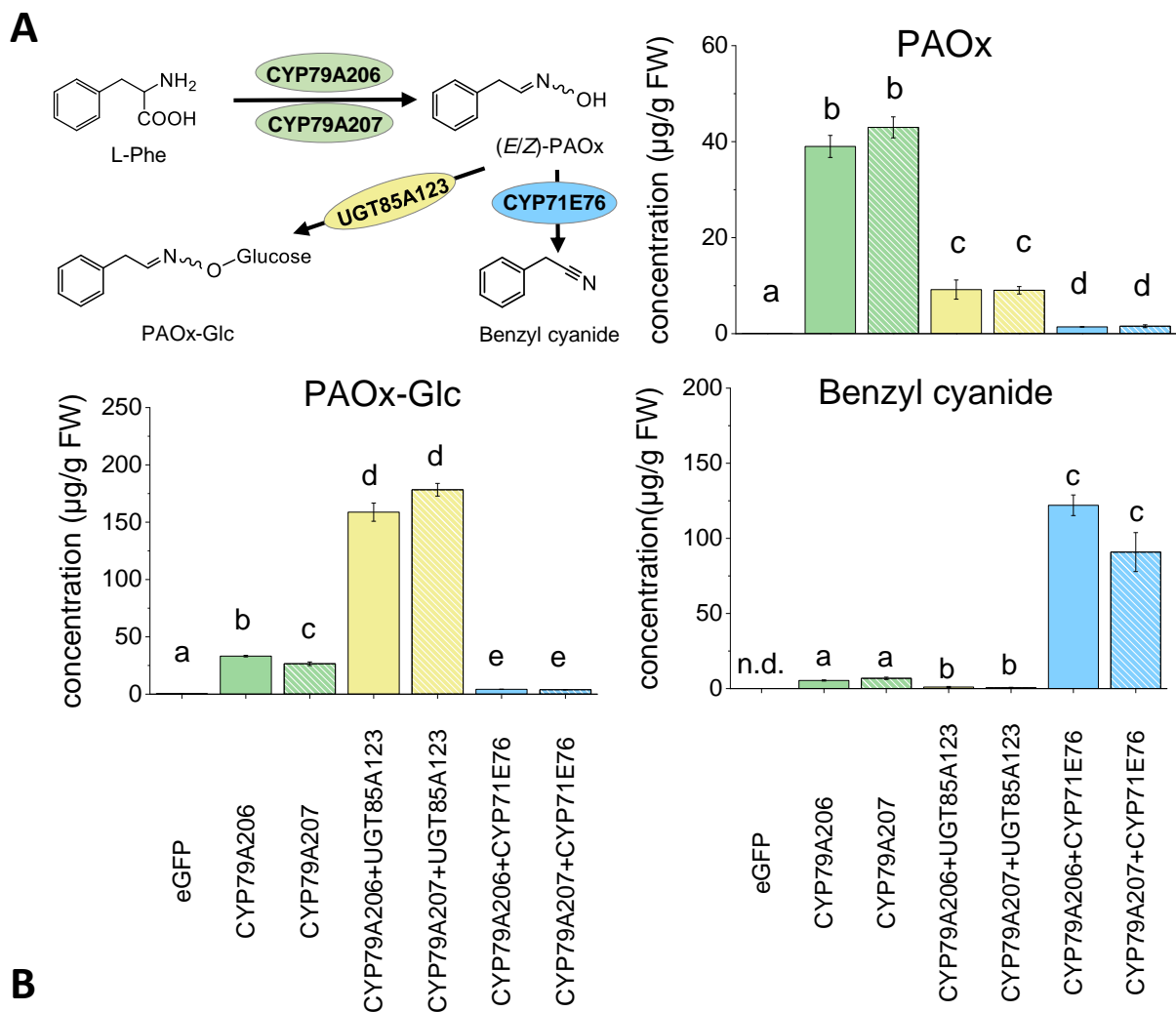
Supplemental Figure S19: Amino acid sequence alignment of candidate UGTs and characterized UGTs from Sorghum and Arabidopsis. The alignment was achieved with the ClustalW algorithm using BioEdit. Black shading corresponds to conserved residues, dark grey shades mark residues identical in six of the sequences, and residues with light grey shading are identical in five of the sequences. Conserved motifs are indicated (Gachon et al., 2005), PSPG: plant secondary product glycosyltransferase.

Substrate	Structure	UGT85A122	UGT85A123	UGT75AB1	UGT76AH1
PAOx		yes	yes	yes	no
salicylaldoxime		yes	yes	yes	no
benzaloxime		yes	yes	yes	no
β -mandelonitrile		yes	yes	no	no
salicylic acid		no	no	yes	no
4-OH-benzoic acid		no	no	yes	no
gallic acid		no	no	yes	no
quercetin		no	no	yes	yes
epicatechin		no	no	no	no
geraniol		yes	yes	no	yes
oct-1-en-3-ol		yes	yes	no	yes

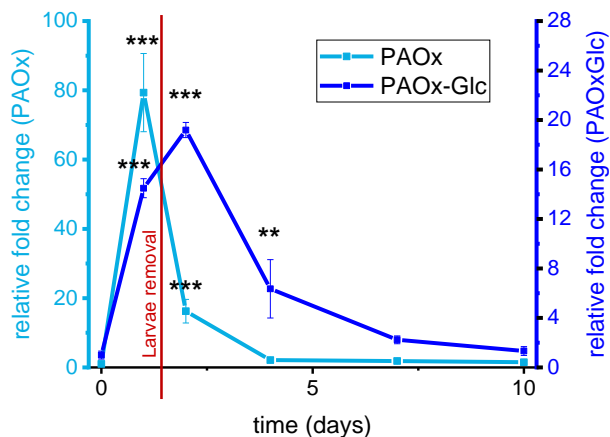
Supplemental Figure S20: Activity of UGT85A122, UGT85A123, UGT75AB1, and UGT76AH1 towards various substrates. Candidate UGT genes were heterologously expressed in *Escherichia coli* and the purified enzymes used for activity assays with various substrates. Compounds were detected with LC-qTOF-MS.



Supplemental Figure S21: Substrate affinity of UGT85A122, UGT85A123, and UGT75AB1 towards PAOx. Heterologous expression in *E. coli* and activity assays showed that three candidate UGTs were able to use PAOx as substrate. To compare their substrate affinities, 10 μg of the purified enzymes were incubated with various concentrations of PAOx for 30 min. Product formation was detected with targeted LC-MS/MS. Means ± SEM are shown (n = 3).

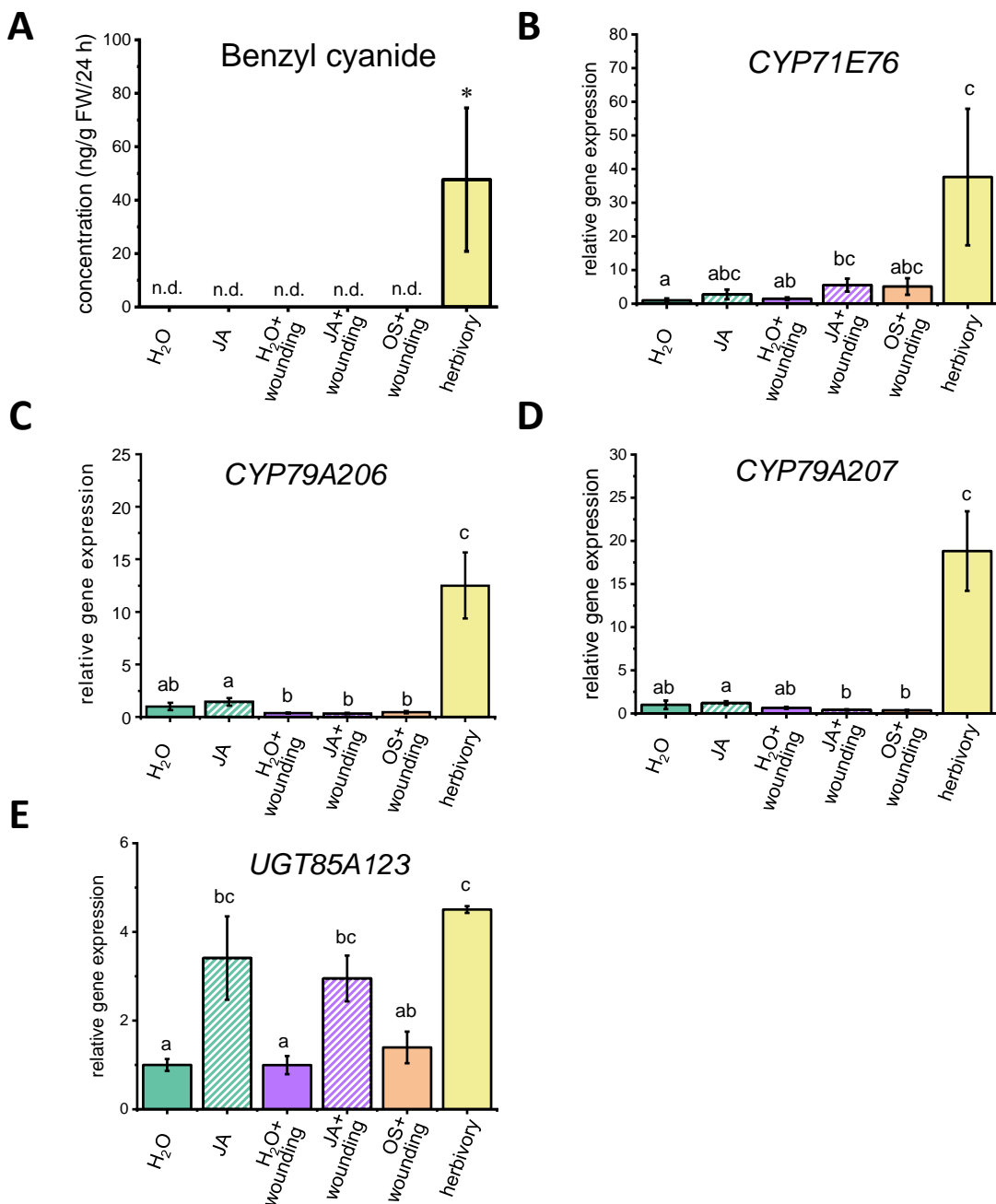


Supplemental Figure S22: Reconstitution of the formation of benzyl cyanide and phenylacetaldoxime glucoside in *Nicotiana benthamiana* by overexpression of tocooca CYP79, CYP71 and UGT genes. *N. benthamiana* was transformed with different combinations of recombinant *Agrobacterium tumefaciens* strains possessing CYP79A206, CYP79A207, CYP71E76, or UGT85A123, respectively. Accumulation of compounds was detected with targeted LC-MS/MS and GC-MS/FID. Means \pm SEM are shown; $n = 4-7$. One-Way ANOVA ($F_{\text{PAOx}} = 372.2$, $p < 0.001$; $F_{\text{benzyl cyanide}} = 32.34$, $p < 0.001$) or linear (gls) model ($L\text{-ratio}_{\text{PAOx-Glc}} = 144.0$, $p < 0.001$) and Tukey *post hoc* test on log transformed data, different letters indicate $p < 0.05$; n.d., not detectable. **(A)** Overview of the pathway and quantification of the compounds of interest in the different plants. **(B)** Chromatogram from GC-MS analysis of the samples. FW, fresh weight. TIC: total ion chromatogram. IS: internal standard.



Supplemental Figure S23: Relative temporal distribution of PAOx and PAOx-Glc in herbivore-damaged *Tococa quadrialata* leaves (see Figure 5).

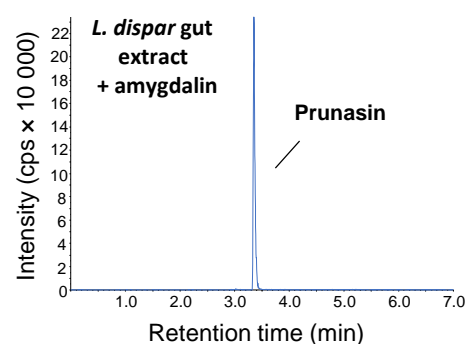
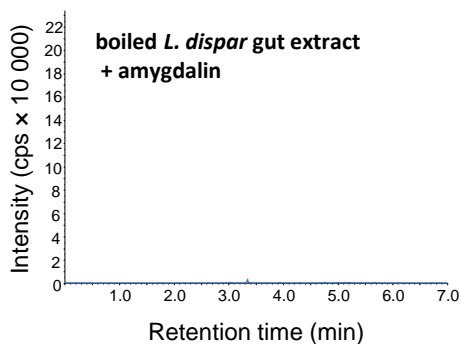
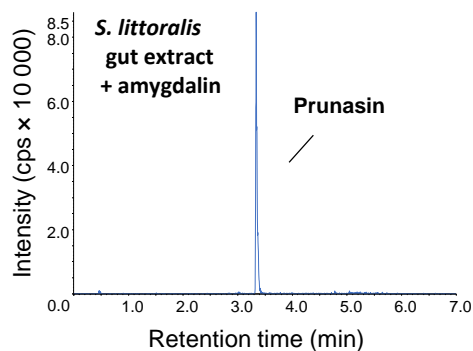
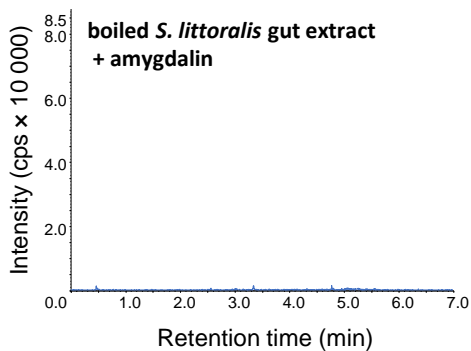
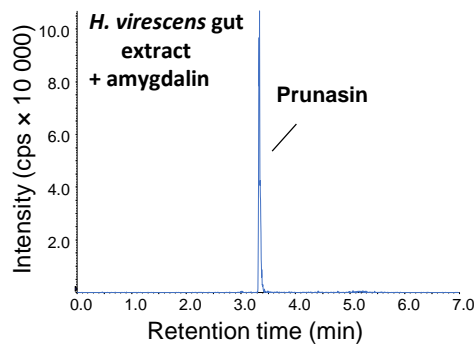
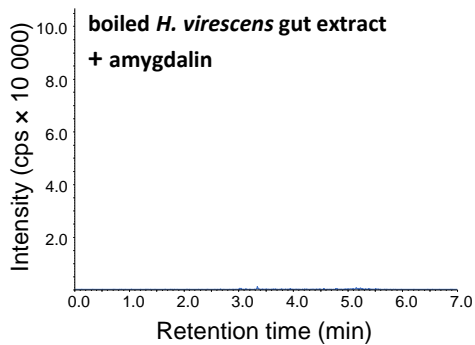
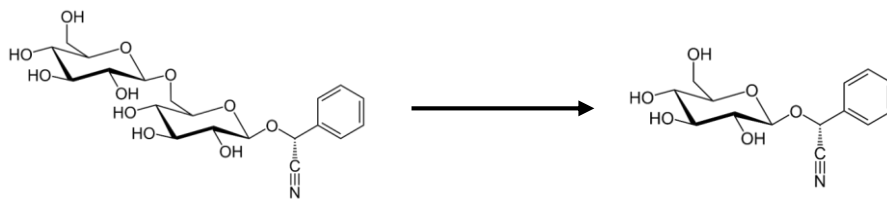
Leaves were exposed to herbivory by *Spodoptera littoralis* caterpillars for 24 hours and the accumulation of PAOx and PAOx-Glc was monitored for ten days. Compounds were extracted with methanol from leaf powder and analyzed using targeted LC-MS/MS. Here, we show the levels of PAOx and PAOxGlc relative to the respective concentration at the start of the experiment (t = 0d). Asterisks indicate significant differences to respective control (0d) based on One-Way ANOVA on log-transformed data ($F_{5,18,PAOx} = 41.03$, $F_{5,18,PAOxGlc} = 12.96$, $p_{PAOx,PAOxGlc} \leq 0.001$) and Dunnett's *post hoc* test. Means \pm SEM are shown; n = 3-5.



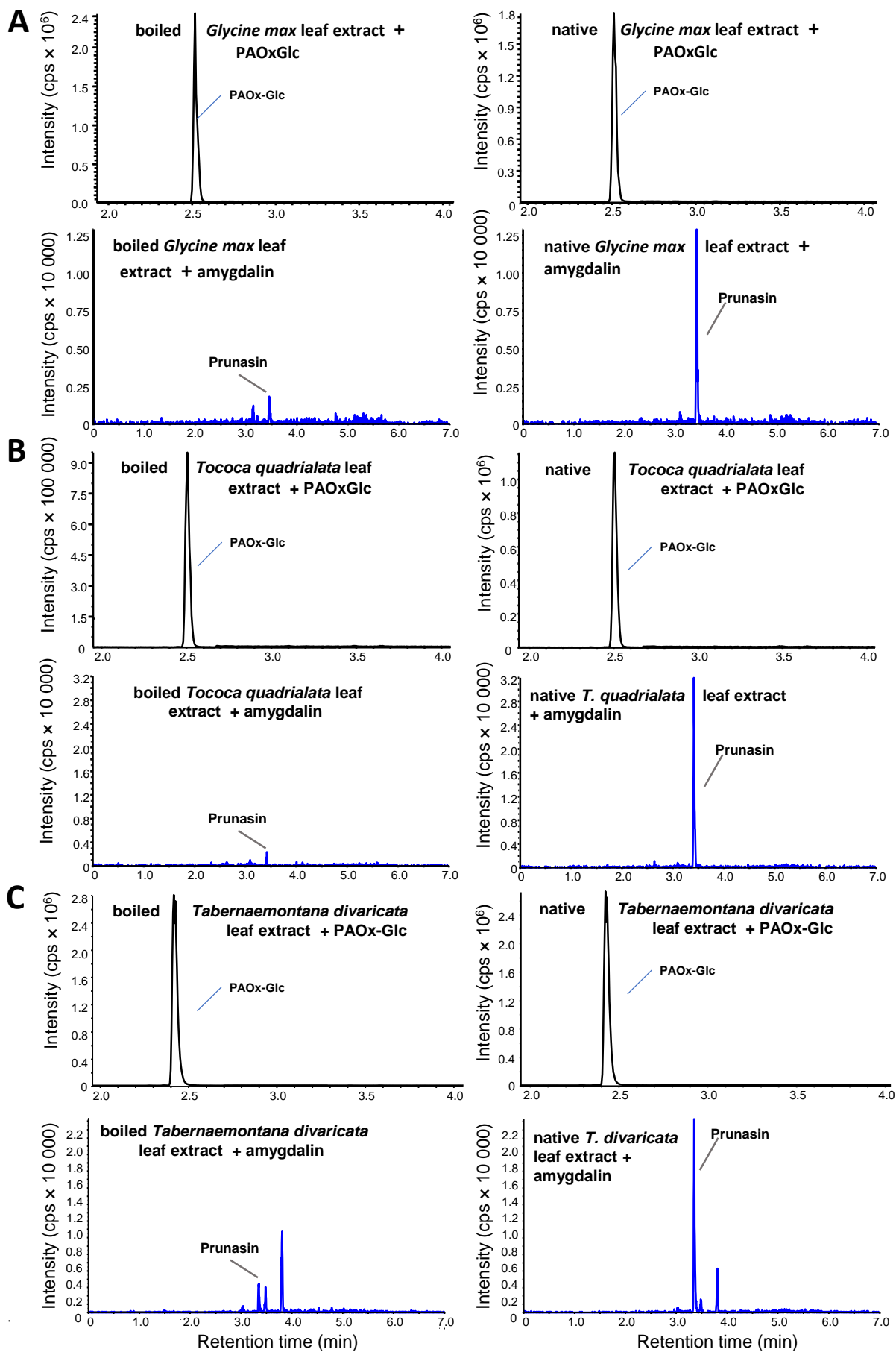
Supplemental Figure S24: Gene expression of *CYP71E76*, *CYP79A206/207*, and *UGT85A123*, and formation of benzyl cyanide in tocooca leaves in response to different treatments (see Figure 6).

Leaves were sprayed with jasmonic acid (JA), oral secretion (OS), or water (H₂O) after mechanical wounding or without further treatment. *S. littoralis* feeding served as a positive control. Volatiles were collected throughout the 24 h (after the) treatment, and quantified by GC-FID (A). Means ± SEM are shown; n = 6-11. Asterisk indicates significant accumulation of benzyl cyanide (> 0) based on Wilcoxon signed rank test, * = p < 0.05. All leaves were harvested 24 h after the (beginning of the) respective treatment, RNA extracted from leaf tissue, transcribed to cDNA, and RT-qPCRs performed (for primers see Supplemental Table S12) with actin as housekeeping gene (B,C,D,E). Relative expression was calculated with the $\Delta\Delta$ Ct method (Pfaffl, 2001). Different letters indicate significant differences (p < 0.05) between treatments based on One Way ANOVAs ($F_{CYP71E76} = 5.842$, p = 0.001; $F_{UGT85A123} = 10.66$, p < 0.001) or GLS linear models (L-ratio_{CYP79A206} = 33.36, L-ratio_{CYP79A207} = 40.15, p < 0.001) analyses on log transformed data and subsequent Tukey *post hoc* tests.

Methodology: cDNA synthesis from 900 ng RNA was performed with the SuperScript™ III First-Strand Synthesis Kit (Thermo Scientific) using oligo (dT)₁₂₋₁₈ primers according to the manufacturer's instructions. The obtained cDNA was diluted 1:10 with ddH₂O. Primer pairs were designed to amplify the respective gene (Supplemental Table S12), and their specificity confirmed by agarose gel electrophoresis, melting curve, and standard curve analysis. Samples were run in an optical 96-well plate on the CFX Connect Real-Time PCR System (Bio-Rad) with the Brilliant III Ultra-Fast SYBR Green QPCR Master Mix (Agilent). PCR conditions are given in Supplemental Table S11. All samples were run in triplicates. Normalized fold expression was calculated with the $\Delta\Delta$ CP method (Pfaffl, 2001).

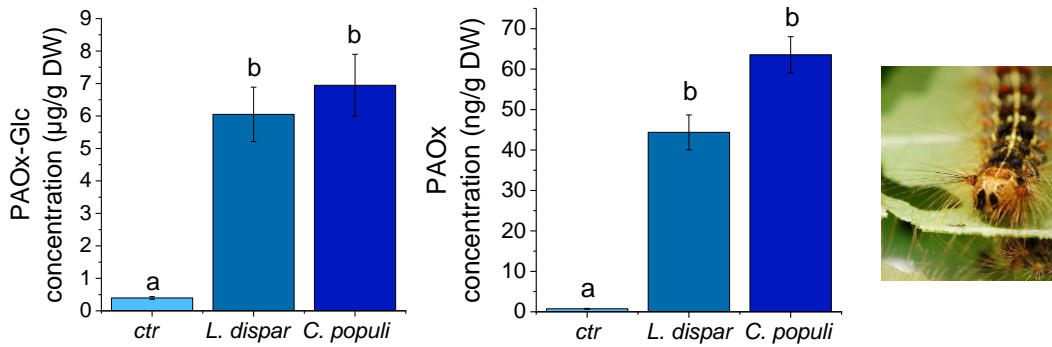


Supplemental Figure S25: Deglycosylation of amygdalin by gut enzymes of different caterpillars. Gut extracts of *Heliothis virescens*, *Spodoptera littoralis*, and *Lymantria dispar* were tested for their ability to form prunasin from amygdalin. Targeted LC-MS/MS analysis revealed glucosidase activities for all tested gut extracts. Boiled extracts were used as negative controls. Cps: counts per second.

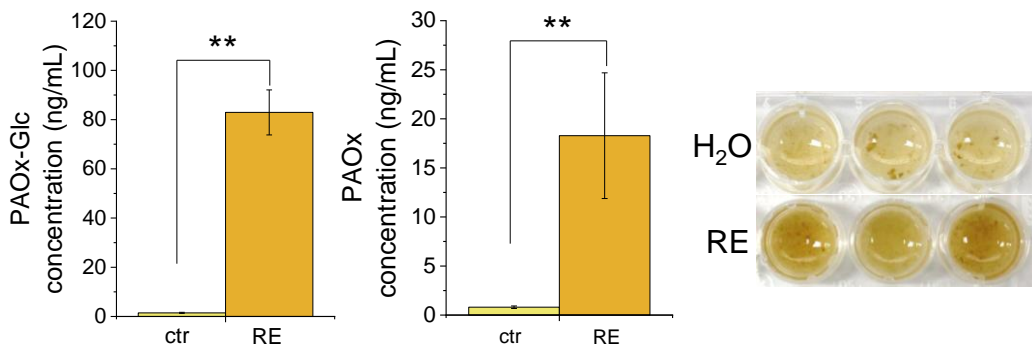


Supplemental Figure S26: Deglycosylation of amygdalin but not PAOx-Glc by crude enzyme extracts of various plant species. Plant extracts of herbivore-damaged leaves of *Glycine max* (A), *Tococa quadrialata* (B), and *Tabernaemontana divaricata* (C) were tested for their ability to form prunasin from amygdalin and PAOx from PAOx-Glc. Targeted LC-MS/MS analysis revealed glucosidase activities towards amygdalin for these extracts. Boiled extracts served as negative controls. Cps: counts per second.

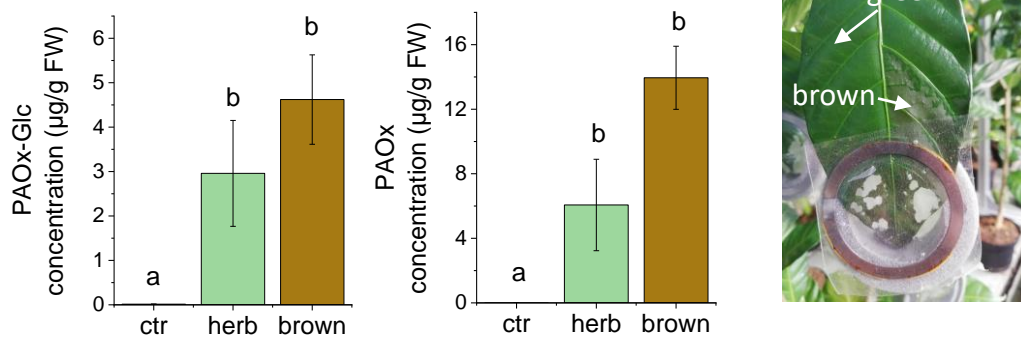
poplar leaves



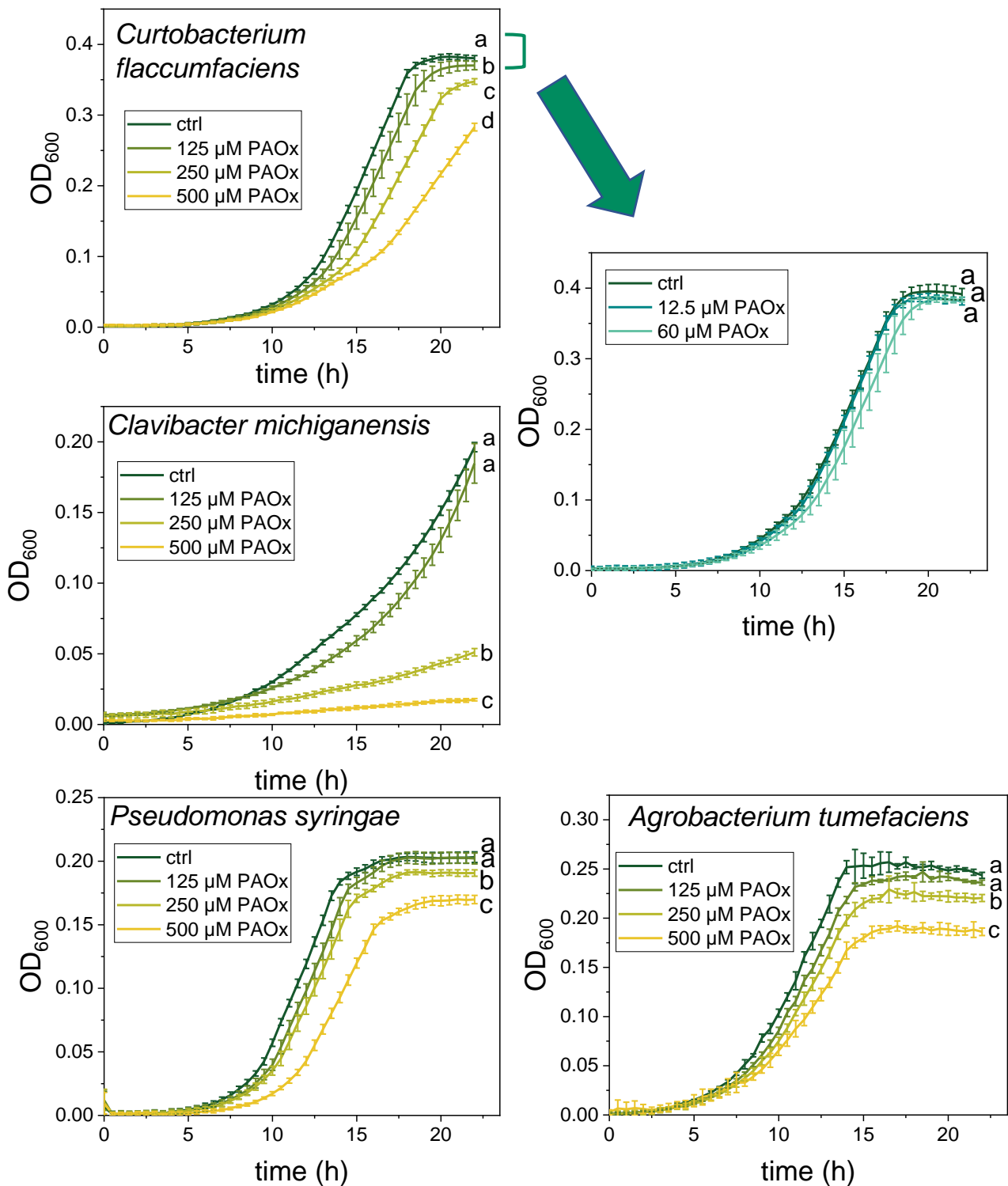
soya cell culture



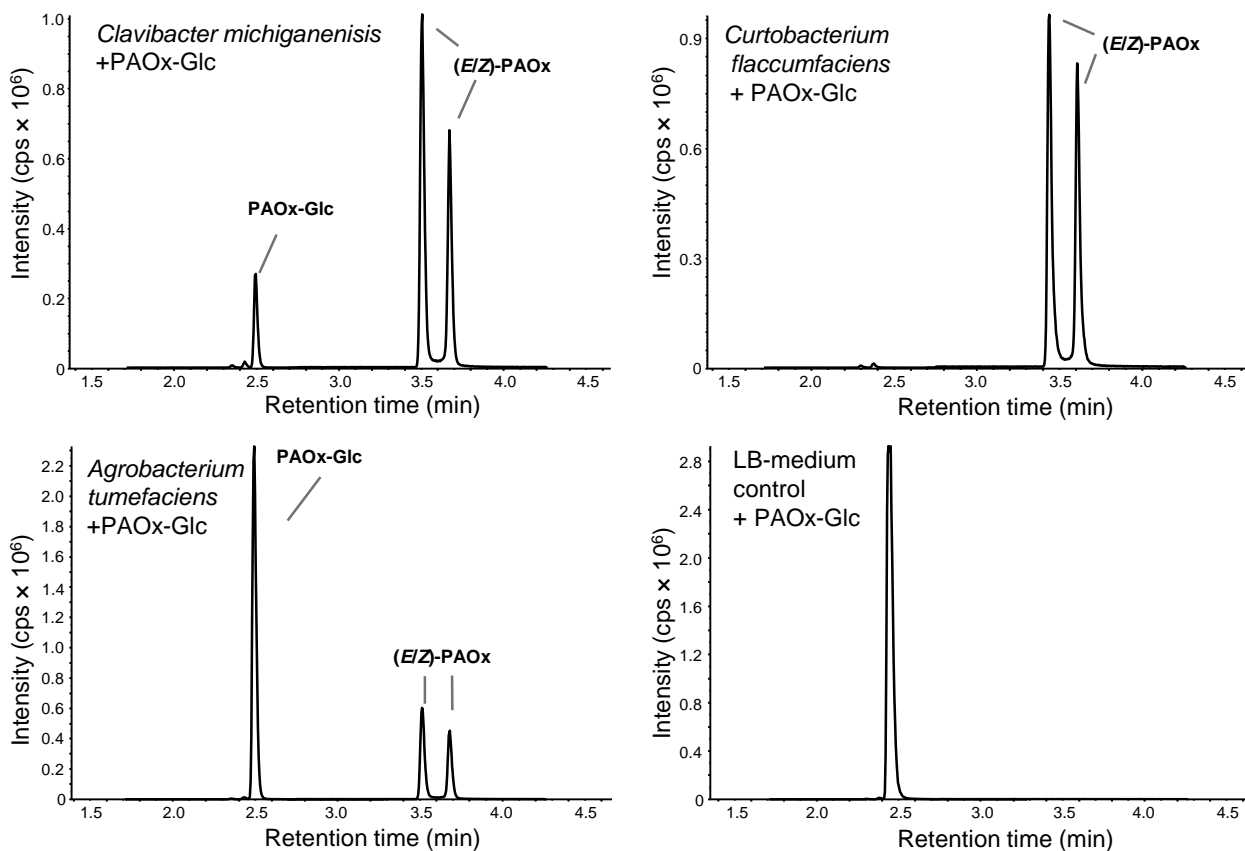
crape jasmine



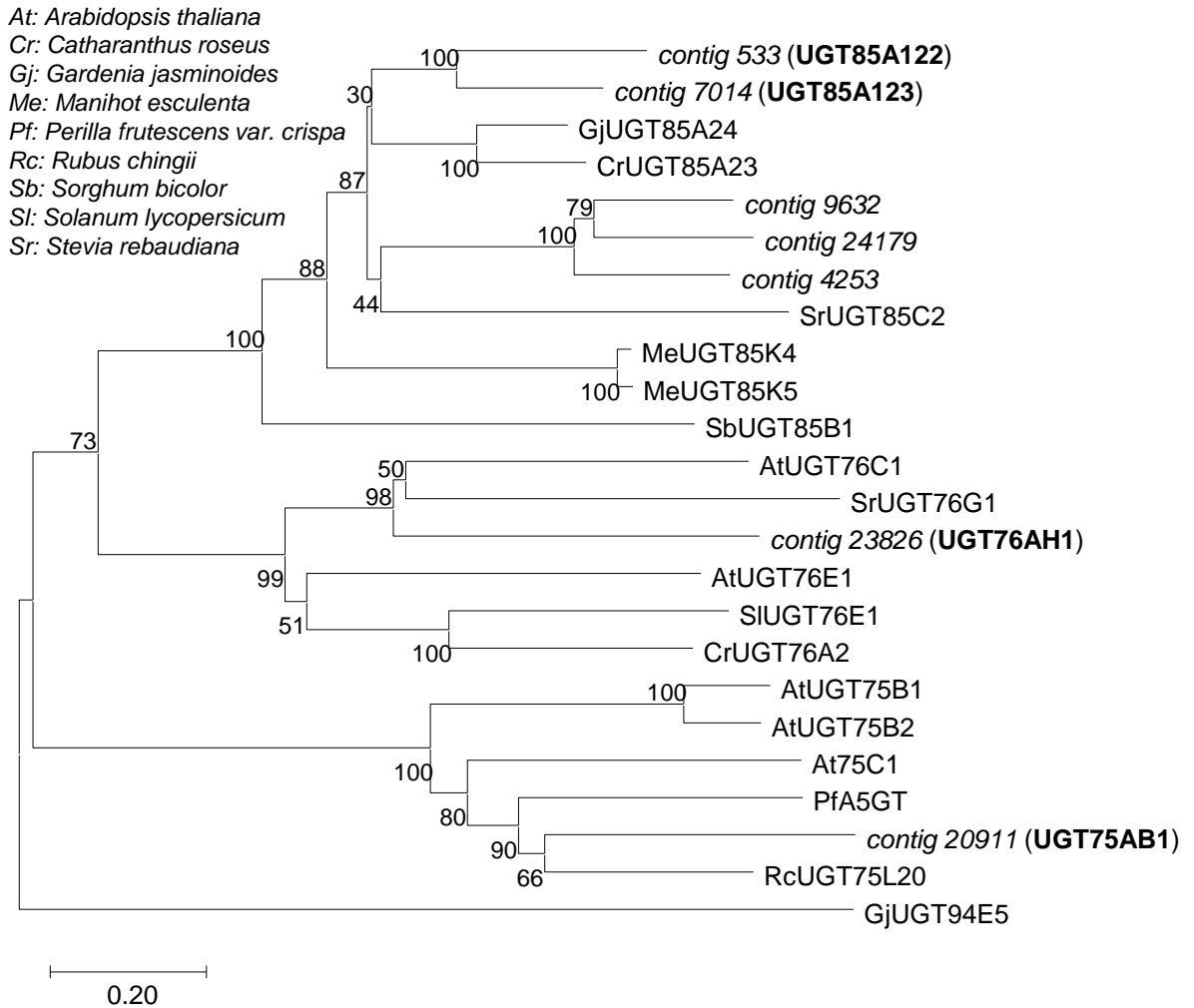
Supplemental Figure S27: Identification of PAOx-Glc in different plant species upon biotic stress. Blue: PAOx-Glc accumulation in Western balsam poplar (*Populus trichocarpa*) leaves upon *Lymantria dispar* and *Chrysomela populi* feeding. Leaves were extracted with methanol and PAOx(-Glc) detected using LC-MS/MS. One-Way ANOVA ($F_{\text{PAOx}} = 411.2$, $p < 0.001$; $F_{\text{PAOx-Glc}} = 125.1$, $p < 0.001$) with Tukey *post hoc* on log transformed data, different letters indicate significant differences ($p < 0.05$); Means \pm SEM are shown; $n = 8$; DW, dry weight. Yellow: soybean cell cultures release PAOx and PAOx-Glc upon induction with raw elicitor (RE) from the oomycete *Phytophthora sojae*. The supernatant of the cell cultures was analyzed using LC-MS/MS. Student's t-test; **: $p < 0.01$; Means \pm SEM are shown; $n = 6$. Green, brown: *Spodoptera littoralis*-wounded leaves of crape jasmine (*Tabernaemontana divaricata*) produce PAOx and PAOx-Glc. Leaves were extracted with methanol and PAOx(-Glc) detected using LC-MS/MS. One-Way-ANOVA ($F_{\text{PAOx}} = 58.06$, $p < 0.001$; $F_{\text{PAOx-Glc}} = 34.38$, $p < 0.001$) with Tukey *post hoc* on log transformed data, different letters indicate significant differences ($p < 0.05$); Means \pm SEM are shown; $n = 3$; FW, fresh weight.



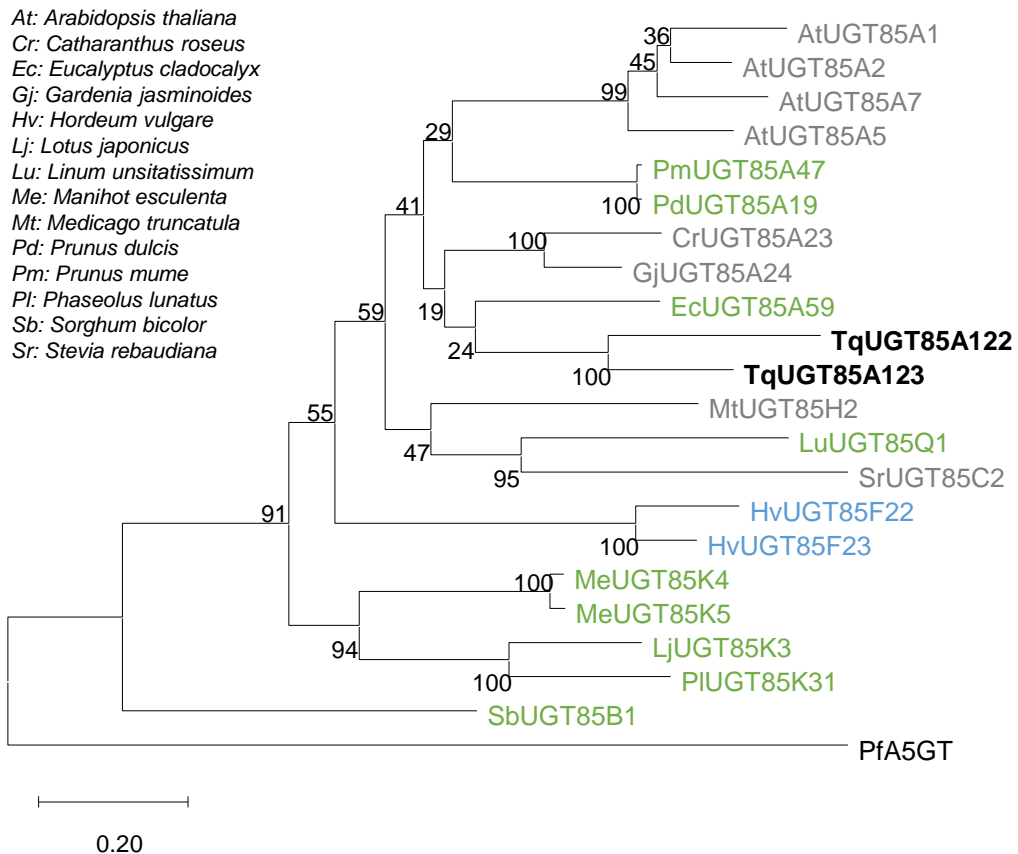
Supplemental Figure S28: Negative effects of PAOx on the growth of several plant pathogenic bacteria. The effect of PAOx on gram-negative (*Agrobacterium tumefaciens*, *Pseudomonas syringae*) and gram-positive (*Curtobacterium flaccumfaciens*, *Clavibacter michiganensis*) bacteria strains was tested in a bacterial growth assay in microtiter plates. Growth of the cultures was monitored over 22 h by measuring the OD₆₀₀ every 30 min. Data are shown as means ± SD; n = 3-6. Different letters indicate significant differences (p < 0.05) between treatments after 22 h. *C. michiganensis*: log transformed; one-way ANOVA ($F_{C.michiganensis} = 1771$, p < 0.001; $F_{A.tumefaciens} = 184.1$, p < 0.001, $F_{P.syringae} = 108.8$, p < 0.001) with Tukey HSD posthoc test or Kruskal-Wallis test ($\chi^2_{C.flaccumfaciens (highconc)} = 20.98$, p < 0.001; $\chi^2_{C.flaccumfaciens (lowconc)} = 3.317$, p = 0.19) followed by multiple pairwise comparisons using Wilcoxon rank sum tests with a Holm correction.



Supplemental Figure S29: Several plant pathogenic bacteria are able to deglycosylate PAOx-Glc. Gram-negative (*Agrobacterium tumefaciens*) and gram-positive (*Curtobacterium flaccumfaciens*, *Clavibacter michiganensis*) bacteria strains were tested for their ability to deglycosylate PAOx-Glc. Bacteria were grown in the presence of PAOx-Glc for 24 h in a microtiter plate, and the LB-medium was analyzed afterwards using liquid chromatography-tandem mass spectrometry (LC-MS/MS).



Supplemental Figure S30: Phylogenetic tree of candidate UGTs from tocooca. The phylogenetic relationship of 7 putative *Tococa quadrialata* UGTs with already characterized UGTs of the respective subfamilies from other plants is shown. The tree was inferred with the Neighbor-joining method and $n = 1000$ replicates for bootstrapping. Bootstrap values are shown next to each node. The scale indicates in the number of substitutions per site. Putative UGTs from tocooca are shown in italics, the characterized ones in bold. GjUGT94E5 (BAK55744.1) was used as an outgroup. UGT: family 1 UDP-glycosyltransferase.



Supplemental Figure S31: Phylogenetic tree of characterized UGTs of the subfamily 85. The phylogenetic relationship of UGT85s involved in the biosynthesis of hydroxynitrile-glucosides with UGT85 using other substrates is shown. The tree was inferred with the Maximum-Likelihood method and $n = 1000$ replicates for bootstrapping. Bootstrap values are shown next to each node. The scale indicates in the number of substitutions per site. The characterized UGT85s from tococha are shown in bold, UGTs involved in the biosynthesis of cyanogenic glucosides in green, of non-cyanogenic hydroxynitrile-glucosides in blue, and those using different compound classes as substrates in grey. PfA5GT (Q9ZR27) was used as an outgroup. UGT: family 1 UDP-glycosyltransferase.

Supplemental Table S1: UGT candidate genes for the glycosylation of PAOx-Glc.

Feature ID	P-value	Fold change	ctr - Mean RPKM	herb - Mean RPKM	UGT sub-family	Length	SWISSPROT: Description	NCBI: Description
contig_533	0.000	7	32	221	UGT85	1928	UGT2_GARJA ame: Full=7-deoxyloganetin glucosyltransferase ame: Full=Genipin glucosyltransferase ame: Full=UDP-glucose glucosyltransferase 2 Short= 2 ame: Full=UDP-glycosyltransferase 85A24	7-deoxyloganetin glucosyltransferase-like
contig_7014	0.000	4	15	67	UGT85	2692	UGT2_GARJA ame: Full=7-deoxyloganetin glucosyltransferase ame: Full=Genipin glucosyltransferase ame: Full=UDP-glucose glucosyltransferase 2 Short= 2 ame: Full=UDP-glycosyltransferase 85A24	7-deoxyloganetin glucosyltransferase-like isoform X1
contig_4253	0.002	2	16	38	UGT85	1657	UGT2_GARJA ame: Full=7-deoxyloganetin glucosyltransferase ame: Full=Genipin glucosyltransferase ame: Full=UDP-glucose glucosyltransferase 2 Short= 2 ame: Full=UDP-glycosyltransferase 85A24	7-deoxyloganetin glucosyltransferase
contig_24179	0.001	6	3	16	UGT85	1176	U85A3_ARATH ame: Full=UDP-glycosyltransferase 85A3	7-deoxyloganetin glucosyltransferase
contig_9632	0.022	5	1	5	UGT85	1630	UGT2_GARJA ame: Full=7-deoxyloganetin glucosyltransferase ame: Full=Genipin glucosyltransferase ame: Full=UDP-glucose glucosyltransferase 2 Short= 2 ame: Full=UDP-glycosyltransferase 85A24	7-deoxyloganetin glucosyltransferase
contig_23826	0.001	15	0	6	UGT76	1597	U76B1_ARATH ame: Full=UDP-glycosyltransferase 76B1	UDP-glycosyltransferase 76C2
contig_329	0.012	2	7	15	UGT76	2943	UGT7_CATRO ame: Full=UDP-glucose iridoid glucosyltransferase ame: Full=UDP-glucose glucosyltransferase 7 Short= 7 ame: Full=UDP-glycosyltransferase 76A2	UDP-glucose iridoid glucosyltransferase
contig_20911	0.007	4	67	237	UGT75	1978	UGT1_GARJA ame: Full=Crocin chloroplastic ame: Full=UDP-glucose glucosyltransferase 1 Short= 1 ame: Full=UDP-glycosyltransferase 75L6 Flags: Precursor	crocin chloroplastic
contig_11576	0.045	3	1	5	UGT75	1121	UGT1_GARJA ame: Full=Crocin chloroplastic ame: Full=UDP-glucose glucosyltransferase 1 Short= 1 ame: Full=UDP-glycosyltransferase 75L6 Flags: Precursor	crocin chloroplastic
contig_5159	0.000	3	17	54	UGT73	1855	SCGT_TOBAC ame: Full=Scopoletin glucosyltransferase ame: Full=Phenylpropanoid:glucosyltransferase 1	scopoletin glucosyltransferase
contig_5158	0.000	5	8	44	UGT73	1042	SCGT_TOBAC ame: Full=Scopoletin glucosyltransferase ame: Full=Phenylpropanoid:glucosyltransferase 1	scopoletin glucosyltransferase
contig_9912	0.045	2	3	8	UGT73	1858	SCGT_TOBAC ame: Full=Scopoletin glucosyltransferase ame: Full=Phenylpropanoid:glucosyltransferase 1	scopoletin glucosyltransferase
contig_9005	0.021	3	3	7	UGT83	1627	U83A1_ARATH ame: Full=UDP-glycosyltransferase 83A1	UDP-glycosyltransferase 83A1
contig_8815	0.003	2	21	47	UGT89	1638	U89A2_ARATH ame: Full=UDP-glycosyltransferase 89A2	UDP-glycosyltransferase 89A2-like

All contigs of the *de novo* assembly encoding glycosyltransferase family 1 type glycosyltransferases with a minimum sequence length of 1000 bp that are significantly upregulated upon herbivore damage ($p < 0.05$, fold change ≥ 2) are listed. Sequences chosen for further characterization are in bold. Selection was based on UGT subfamily, RPKM values and fold change in herbivore-damaged samples.

Supplemental Table S2: Growth conditions for *Tococa quadrialata*.

Greenhouse conditions	
<i>Temperature</i>	
Day:	23-25 °C
Night:	16-18 °C
Humidity	70%
Light/dark cycle	16 h/8 h
composition of the soil	
<i>Percentage</i>	<i>Material</i>
25%	Klasmann potting substrate (Klasman-Deilmann, Geeste, Germany)
25%	Latvian white peat
25%	pine bark (7-15 mm)
12.5%	Legaton (5-7 mm)
12.5%	sand
Inoculated with	BioMyc™ Vital Mykorrhiza (BioMyc, Brandenburg, Germany).

Supplemental Table S3: Chromatographic gradients for the analysis of jasmonates, aldoximes, and prunasin using an LC-TripleQuad-MS system.

Gradient	HPLC	Solvents (A/B)	Flow (µl/min)	Time (min)	Temperature (°C)	Solvent A (%)	Solvent B (%)
A1	Agilent 1200	0.2% FA in ddH ₂ O (A), Acetonitrile (B)	1100	0 4 4.1 5 5.1 8	25 °C	90 30 0 0 90 90	10 70 100 100 10 10
A2	Agilent 1260	0.05% FA in ddH ₂ O, Acetonitrile (B)	1100	0 4 4.1 5 5.1 8	20 °C	90 30 0 0 90 90	10 70 100 100 10 10
B	Agilent 1260	0.05% FA in ddH ₂ O, Acetonitrile (B)	1100	0 0.5 4 4.1 4.5 4.6 7	20 °C	95 95 50 0 0 95 95	5 5 50 100 100 5 5
C	Agilent 1260	0.05% FA in ddH ₂ O, Acetonitrile (B)	1100	0 0.5 6 6.02 7.5 9.5 9.52 12	20 °C	95 95 62.6 80 0 0 95 95	5 5 37.4 80 100 100 5 5

All separations were achieved on a Zorbax Eclipse XDB C18 column (50 mm 4.6 mm, 1.8 µm, Agilent Technologies). For MS parameters, see Supplemental Table S4.

Supplemental Table S4: MRM parameters for the LC-MS/MS analysis of jasmonates, aldoximes, and prunasin using an LC-TripleQuad-MS system.

compound	Mass spectrometer	mode	HPLC gradient	Q1	Q3	DP (V)	CE (V)	Retention time (min)
(E/Z)-phenyl-acetaldoxime	API5000	pos	A1	136.1	119.1	56	17	3.5; 3.7
	API6500	pos	A2	136.1	119.1	30	17	3.4; 3.6
Phenylacetaldoxime glucoside	API5000	pos	A1	298.0	136.0	70	13	2.5
	API6500	pos	A2	298.0	136.0	30	13	2.5
Prunasin	API6500	neg	B	340.0	59.0	-40	-56	3.4
JA	API6500	neg	C	209.1	59.0	-30	-24	7.2
D ₆ -JA	API6500	neg	C	215.1	59.0	-30	-24	7.2
D ₅ -JA	API6500	neg	C	214.1	59.0	-30	-24	7.2
JA-Ile	API6500	neg	C	322.2	130.1	-30	-30	7.3
D ₆ -JA-Ile	API6500	neg	C	328.2	130.1	-30	-30	7.3
D ₅ -JA-Ile	API6500	neg	C	327.2	130.1	-30	-30	7.3

All separations were achieved according to Supplemental Table S3.

Supplemental Table S5: Non-target metabolite analysis by LC-ESI-Q-ToF-MS.

Chromatographic gradients for untargeted metabolite analysis using ultra-high-performance liquid chromatography–electrospray ionization– high resolution mass spectrometry (UHPLC–ESI–HRMS)							
HPLC	column	Solvents (A/B)	Flow (µl/min)	Time (min)	Temperature (°C)	Solvent A (%)	Solvent B (%)
Dionex Ultimate 3000 series UHPLC (Thermo Scientific)	Zorbax Eclipse XDB-C18 column (100 mm x 2.1 mm, 1.8 µm, Agilent)	0.1% FA in ddH ₂ O (A), Acetonitrile (B)	300	0	25 °C	95	5
				0.5		95	5
				11		40	60
				11.1		0	100
				12		0	100
				12.1		95	5
15	95	5					
Parameters of the Bruker timsToF mass spectrometer (Bruker Daltonics, Bremen, Germany)							
Mode	Capillary voltage (kV)	End plate offset (V)	Nebulizer pressure (bar)	Drying gas	Acquisition (Hz)	Mass range (m/z)	Data processing software
positive	4.5	500	2.8	Nitrogen (8L/min, 280°C)	12	50-1500	MetaboScape (Bruker Daltonics)
negative	-3.5	500	2.8	Nitrogen (8L/min, 280°C)	12	50-1500	MetaboScape software (Bruker Daltonics)

At the beginning of each chromatographic analysis 10µL of a sodium formate-isopropanol solution (10 mM solution of NaOH in 50/50 (v/v) isopropanol- water containing 0.2% formic acid) was injected into the dead volume of the sample injection for recalibration of the mass spectrometer using the expected cluster ion *m/z* values.

Supplemental Table S6: Temperature profile of benzyl cyanide measurements by GC-FID and GC-MS.

hexane extracts		
Initial temperature	60°C	2 min
Ramp I	60°C	
	↓	6°C/min
	160°C	
Ramp II	160°C	
	↓	60°C/min
	300°C	
Final temperature	300 °C	2 min

Supplemental Table S7: Parameters used for the *de novo* assembly.

Assembly parameters	
Word size	35
Bubble size	650
Quality of the <i>de novo</i> assembly	
total contigs	49,957
N50	1,659
Complete BUSCOs*	78.5%
Missing BUSCOs*	10.2%
Annotation	
BLAST2GO#	Swiss-Prot, NCBI

*Benchmarking Universal Single-Copy Orthologs (BUSCO) analysis (<https://busco.ezlab.org/>, last accessed on 04.02.2022; (Simao et al., 2015))

#(Gotz et al., 2008)

Supplemental Table S8: Primers used for cloning.

Name	Sequence	Usage
CYP79A206_subc_fwd	ATGAATATTTCTGCTTCCGCC	cloning, in pJET1.2/blunt
CYP79A206_subc_rev	CTAGAATGACGGGTAAAGGTG	cloning, in pJET1.2/blunt
CYP79A207_subc_fwd	ATGAATATTTCCGCTTACGC	cloning, in pJET1.2/blunt
CYP79A207_subc_rev	CTAGAATGATGGGTAAAGGTG	cloning, in pJET1.2/blunt
CYP71E76_subc_fwd	ATGTCTTCTACAATTATTTCTTC	cloning, in pJET1.2/blunt
CYP71E76_subc_rev	TTAATTATATTTAGTTGGAACCAAACG	cloning, in pJET1.2/blunt
UGT85A123_subc_fwd	ATGAGTTCTGAACAAGAAGCAGAGC	cloning, in pJET1.2/blunt
UGT85A123_subc_rev	TCATTGCTCGGAAAGAAGCAGTG	cloning, in pJET1.2/blunt
CYP79A206_NotI_fwd	CAAGCGGCCGCAATGAATATTTCTGCTTCCG	cloning, in pESC-Leu2d
CYP79A206_PacI_rev	GCTTTAATTA ACTAGAATGACGGGTAAAGGTG	cloning, in pESC-Leu2d
CYP79A207_SpeI_fwd	AAGACTAGTA AATGAATATTTCCGCTTACGC	cloning, in pESC-Leu2d
CYP79A207_SacI_rev	ACAGAGCTC CTAGAATGATGGGTAAAGGTG	cloning, in pESC-Leu2d
CYP71E76_SpeI_fwd	TAAACTAGTA AATGTCTTCTACAATTATTTCTTC	cloning, in pESC-Leu2d
CYP71E76_SacI_rev	ACGGAGCTC TTAATTATATTTAGTTGGAACCAAAC	cloning, in pESC-Leu2d
CYP79A206_USER_fwd	GGCTTAAU ATGAATATTTCTGCTTCCGCCG	cloning, in pCAMBIA2300U
CYP79A206_USER_rev	GGTTTAAU CTAGAATGACGGGTAAAGGTGC	cloning, in pCAMBIA2300U
CYP79A207_USER_fwd	GGCTTAAU ATGAATATTTCCGCTTACGCCG	cloning, in pCAMBIA2300U
CYP79A207_USER_rev	GGTTTAAU CTAGAATGATGGGTAAAGGTGC	cloning, in pCAMBIA2300U
CYP71E76_USER_fwd	GGCTTAAU ATGTCTTCTACAATTATTTCTTCCC	cloning, in pCAMBIA2300U
CYP71E76_USER_rev	GGTTTAAU TTAATTATATTTAGTTGGAACCAAACGC	cloning, in pCAMBIA2300U
UGT85A123_USER_fwd	GGCTTAAU ATGAGTTCTGAACAAGAAGCAGAGC	cloning, in pCAMBIA2300U
UGT85A123_USER_rev	GGTTTAAU TCATTGCTCGGAAAGAAGCAGTG	cloning, in pCAMBIA2300U
UGT76AH1_pET100_fwd	<u>CACCATGGGCACAACCTCAAGTCAAG</u>	cloning, in pET100
UGT76AH1_pET100_rev	TTATAATTTTCCGTTGGCATGAG	cloning, in pET100

Primer name indicates the gene to be amplified. The important sequence motif for cloning in the respective vector is underlined or in bold

Supplemental Table S9: Codon-optimized ORF of tocoxa UGTs for expression in *Escherichia coli*.

Encoded enzyme	Codon optimized nucleotide sequence
UGT85A122	<p>ATGGCACGTGATAGCGCAGTTGAAGCACTGCCTGGCACCAAACCGCATGCAATTATTGTTCCGATATCCG GCACAGGGTCATATTAATCCGCTGCTGAAACTGGCAAAAATTCTGCATGGTCGTGGTGGTTTTTCATGTGA CCTTTGTTAATACCGAATATAACGCACGTCGTCTGCTGCGTAGCCGTGGTCCGACCAGCCTGGATGATAT GCCAGGTTTTCATTTTGAAACCATTCCGGATGGTCTGCCTCCGGTTGATGCAGATGTTATGCAGGATGTT CCGGCACTGAGCGATAGCCTGAGCCGTACCTGTTTTGAACCGTTTGTGAACCTGGTTAGCAAAGTGAATC AGCATGGTGGTCCGCCTGCAACCTGCTTTGTTTTATGATGCAATGATGCCGTTTGTGGCAGATGCAGCAG AAAAATTTGGTCTGCCAGCAGTTGCATTTTGGCCTCCGGCAGCATGTGCAATTTGGGGTGTTCACAGTA TCCGAAACTGATTGAAAAAGTCTGGTCCGCTGAAAGATAGCAGTTATCTGAGCAATGGTTTTCTGGAT ACCGTGATTGAATGGATTCCGGGTATTGATAATTTTCCGCTGCGTGATATCCGACCTTTATTCAGACCAC CGATCCGAATGATATTATGGTGCATTACATGATTCGTAGCGTTGAAGTGAGCAGAAAAAAGCATGGTCC GTTGTGTTAATACCTTTGATGCACTGGAAGCAGATGTTCTGCGTGCACTGAAAAGCATTATCCGAGCAT TTATACCGTTGGTCCGCTGAATCTGGTCTGGATCGTTATCCGGAAGAAGAAGTACCCGACGTTGGTAGC AATCTGTGGAAGAAGATAATAGCTGTCTGAAATGGCTGGATAGCCAAGAAGTGGTAGCGTTGTTTTATG TGAATTTGGTAGCATTACCGTTGCAACCGCAGAGCAGATGACCGAATTTGACGGGTTTAGCAAGTAG CCGATGCCGTTTCTGTGGGTTATTCGTCGGATCTGGTGTGGTGAAGCGCAGTGCTGCCACCGGG TTTTACCGATGAAACCAGCGATCGTTGTATGATTAGCGGTTGGTGTCCGCAAGAAGAAGTTCTGAAACAT CCGAGTATTGGTGGCTTTCTGACCCATAGTGGTTGGAATAGCACCTGGAAAAGCATGAGTGCCGGTGT CCGATGGTTTTGTTGGCGTTTTTGGCCGATCAGCAGACCAATTTGGTATGGTAAAAAAGCATGGGGTA TCGGCATGGAATTTGATCATGATGTGAAACGCGATAAAGTGAAGGTATGGTTAAAGAAGTATGGAAGG TGAAAAGGGCAAAGAATGAAACGTCGTGCAGCAGGTTGGCGTAGCGCAGCCGAAAAAGCAGTTGCC CTGGTGGTAGCAGCTATAAAAACTGGAAAACTGCTGAGCCTGCTGCTGCCGAAAAAATGA</p>
UGT85A123	<p>ATGAGCAGCGAACAAGAAGCAGAGCATGAAAACCCATGTTTCATCCGAATCCGAAACCGCATGCAGTTTTA TCCGATCCCGGCACAGGGTCATATTAATCCGATTTCTGAAACTGGCAAAAAGTGGTATGTTGTCATGG CCTTCATGTTACCTTTGTGCATACCGAATATAACCATCGTCGTCTGCTGCGTAGCCGTGGTCCGGATAGC CTGCTGGGTCTGCCTGGTTTTCGTTTTGAAACCATTCCGGATGGTCTGCCTCCGACACCGGAAGATGCA AGTGATGATGTTACCCAGGATATCCGAGCCTGTGTGATAGCACCAGCCGTACCTGTACCCGACCCGTTTA TTAGCCTGGTGCCTGCTGAATGCCGAAGAAGTGGTCCGCCTGTTAGTGTGTTTTGATGATGTG CAATGAGCTTTGCACTGGATGCAGCCGAAGAATTTGGTGTTCGGGGTGTTCATATTGGACCCCGAGCG CATGTGGTGTCTGGCATATAGCTATTATCATAAGCTGGTCGAAAAAGGTCTGAGTCCGCTGAAAGATAG CAGTTATCTGACCAATGGTTATCTGGATACCGTTGTTGATTGGATTCCGGGTATGAAAAAATCATTGTC TGCGTATCTGCCGAGCTTTATTCGTACCACCGATCCGAATGATGTGATGGTGAATTTGATGGTGGCG AATTCAGCTACCAGCCAGAAAAGCAGCGCACTGGTTCTGAATACCTTTGACAAAAGTGAAGAAAGATGTT CTGGATGCACTGAGCGCAATTTTTCCGAGCGTTTATGCAATTTGGTCCGATTAATCTGATGCTGGATCGT TTAGTGATGAAGATCTGGATAGCATTGGTAGCAATCTGTGGAAGAAGAAAATTTGGTGTCTGCATTGGCT GGATAGCCAGGATCTGGGTAGCGTTATTTATGTTAATTTGGCAGCATTACCGTGCCAACCAAGAGCAG ATTACCGAATTTGCATGGGGTTTAGCAGATAGCAAAAACCGTTTTCTGTGGGTTATTCGTCGGGATCTGG TTATTGGTGAAGCGCAGTTCTGCCTCCAGTTTTGGTGTGCAACCGAAGGTGCTGGTATTCTGAGCG GTTGGTGTCCGCAAGAAGTGGTGTGAAACATCCGAGCATTGGTGGTTTTCTGACCCATTGTGGTTGGAA TAGCATGATGGAAGCGTTTTGAGCGGTGTCGGGTTATTTGTTGGCCGTTTTTGCAGAACAGCAGACC AATTGTTGGTATGGTAAAAATGCCTGGGGTATTGGCATGGAATTTGATAATGAAGTGAACCGCAGCAAG TTGAAGGTATGGTTCGTGAAGTGTGGATGGCGAAAAAGGCAAGAAGTGAACCGTGTGCAGCAGAAT GGAAAGCAGCCGAGAAAGAGCAGCAGCACCTGGTGGTAGCAGCCATCAGAATCTGGAAAAAGTGGT GCACTGCTGCTGAGCGAACAGTAA</p>
UGT75AB1	<p>ATGGCACCGCCTAATTTCTGCTGGTTACCTTTCTGGTTCAGGGTCATATTAATCCGAGCCTGCGTTTTG CAGAACGCTGATTTCGATTTGGTGTGATGTTACCTTTACCACCGCACTGAGCGCAGTCGTGATGAG CGATAGCAAAAAGCCCTCCGCCTGAAGGTCTGAGTTTTGCAACCTTTAGTGATGGTTATGATGAGGGCATT AAAGAAGCAGAACTGGATCTGGATGTGATATGAAAGAAATACCCGTCGTGGTCCGGAACACTGCGT GAACTGATTCTGGAACACGTGATCGTGGCACCATTTTACCACATCTTTTTACCATTCTGATGCCGTG GGCAGCAGATGTTGCACAGAGCCTGGGTCTGCGTAGCACCTGGTTTGGATTGAGCCTGCAACCGTTTT TGATATCTACTACTATCACTTCAACGGCTATGACCAGCTGATTGTTCAAGCGCAGATGCAGCAGCAGCC GATAATGGTATAGCCGTGAAATTCGTCTGCCTGGTATGCTGCCGATGACCAGCAGCTATTTCCGAGCT TTCTGGCAAGCGGTAATCAGTATCATTTTTCACTGCCGGTATCAAACGCCATTTTGAATTTCTGAATAGC GAAAAACCGGCACCATGAAACCGAAAGTTCTGGTTAATACCTTTGAAGAAGTGAAGTGAACCGCAGCAAG AAGCAATTGATGAACTGAATGTTATCCGGTGGTCCGTTTTATCCGCTGGCATTCTGGATGAACAGCA TCCGACCGATACCAGCTTAGGTGGTACCTGTTTCAGAAAAGCCGTGATCTGGATTATTTGACTGGCTG AATAAACAGCAGGCAGCAAGCGTTATCTATATTAGCTTTGGTAGCCTGAGCCTGTTAGCCGTCGCGAGA AAGAAGAAATGGCAAAAGCACTGATTGCAATGGGTCCGTTTCTGTGGGTTATTCTGAGGTTAGGTTGGG TGAAGAAGAGGAAAGAGGACGATAAACTGAGCTATGAAGAAGAAGTGAAGCAAACTGGGTATGATTGTTCC GTGGTGTAGCCAGGTTGAAGTCTGAGCAATCCGAGCGTTGGTGTGTTTTGTTACCCATTGTGGTTGGAAT AGCACCAGCGAAAGCCTGGTTTTGGTGTTCGAGTGGTGGTTTTCCGCAGTGGTCAGATCAGCAGACCC AATGCAAACTGGTTGAAGAGGTTTGGCTACCGGTGTTCAAGTTGGTAAAGGCAATGGTGAAGTGT GTTGAAGCCGGTGAATTTGAACGTTGTCTGGAAGTTGTTTTAGGGTATGGTGAAGGCAAGGTCGTAAGTGC GTGGTATGCAAAAAATGGGGTGAAGTGGCAAAAAAGCAGCAAAAGATGGTGGTAGCAGCGATAATA ATCTGCGTCTTTTTGTTGATGGTCTGGTTAAAGGCACCGCAAGCAGCGAATAA</p>

Supplemental Table S10: Buffers.

Name	Ingredients	pH
UGT resuspension buffer	50 mM disodium hydrogen phosphate	7.4
	500 mM sodium chloride	
	10 mM imidazole	
	10% glycerol	
	10 ⁻² v/v protease inhibitor Mix HP (SERVA, Heidelberg, Germany)	
	10 ⁻⁴ v/v Novagen® Benzonase® Nuclease (Merck)	
25,000 U/ml lysozyme (AppliChem, Darmstadt, Germany)		
UGT assay buffer	50 mM Tris-HCl	7.5
	10% glycerol	
Gut protein extraction buffer	50 mM citric acid	6.5
	100 mM disodium hydrogen phosphate	
	5×10 ⁻³ v/v protease inhibitor Mix HP (SERVA)	
Tococa protein extraction buffer	25 mM HEPES	7.2
	3% PVPP	
	1% PVP	
	4% Amberlite XAD4	
	1 mM EDTA	
	5 mM Na ₂ HSO ₃	
	5 mM DTT	
5×10 ⁻³ v/v protease inhibitor cocktail III (Calbiochem)		
Glucosidase assay buffer	50 mM citric acid	6.5
	100 mM disodium hydrogen phosphate	
Infiltration buffer	10mM MES	5.7
	10mM MgCl ₂	
	100 μM acetosyringone	
LB selection media	LB media	n.a.
	50 μg/ml kanamycin	
	10 μg/ml rifampicin	
	25 μg/ml gentamicin	

Supplemental Table S11: Thermocycler program for RT-qPCR.

Phase	Time		Temperature	
	Figure S24	Figure S13		
Initial denaturation	3 min	3 min	95 °C	} 40x
denaturation	10 s	20 s	95 °C	
Annealing and extension	10 s	20 s	60 °C	
Plate read				
Final denaturation	1 min	1 min	95 °C	
Melting curve	5 s	5 s	55 °C → 95 °C	

Supplemental Table S12: List of primers used for RT-qPCR.

Name	Sequence	Amplicon length
CYP79A206_qPCR_fwd	CGACCTTCGTGTTACTTTACGC	140 bp
CYP79A206_qPCR_rev	ACGGGCTTGTTAGAGAGCATC	140 bp
CYP79A207_qPCR_fwd	ACCTTCGTCGTGCTTTACGC	150 bp
CYP79A207_qPCR_rev	TCCAACGGAACACTGGCTTG	150 bp
CYP71E76_qPCR_fwd	CGGAAACCTTCACCAACTCGG	140 bp
CYP71E76_qPCR_rev	GCACCTCCTTAGCCATCTCG	140 bp
UGT85A123_qPCR_fwd	CCCCCGTTAGTTGCGTAGTG	200 bp
UGT85A123_qPCR_rev	CGACCGTGTCCAAGTATCCGT	200 bp
UGT85A122_qPCR_fwd	ATCCCCACATTCATCCAGACGACC	140 bp
UGT85A122_qPCR_rev	CGACTTCAAGGCACGCAGAAC	140 bp
UGT75AB1_qPCR_fwd	TTCAACCCGCCACCGTCTTC	300 bp
UGT75AB1_qPCR_rev	GCCTTCACCGCTTCTGCCT	300 bp
Actin_fwd	CTCTGGTGATGGTGTCAGTCAC	140 bp
Actin_rev	TGTAACCCCTTTTCGGTGAGG	140 bp

Supplemental Table S13: Accession numbers of known enzymes that were used for the construction of the phylogenetic trees.

Name	Accession number	Plant species	Name	Accession number	Plant species
CYP79 enzymes					
AtCYP79A2	ANM70027.1	<i>Arabidopsis thaliana</i>	MeCYP79D1	AAF27289	<i>Manihot esculenta</i>
AtCYP79B2	AEE87143.1	<i>Arabidopsis thaliana</i>	PtCYP79D6	AHF20912	<i>Populus trichocarpa</i>
AtCYP79F1	AEE29448	<i>Arabidopsis thaliana</i>	PtCYP79D7	AHF20913	<i>Populus trichocarpa</i>
AtCYP79F2	AAG24796	<i>Arabidopsis thaliana</i>	JaCYP79A68	BAP15883.1	<i>Prunus mume</i>
EcoCYP79D62	AOW44274	<i>Erythroxylum coca</i>	JaCYP79D16	BAP15884.1	<i>Prunus mume</i>
EfCYP79D60	KX344462	<i>Erythroxylum fischeri</i>	SaCYP79B1	AAD03415	<i>Sinapis alba</i>
EcCYP79A125	AYN73067	<i>Eucalyptus cladocalyx</i>	SbCYP79A1	AAA85440.1	<i>Sorghum bicolor</i>
LjCYP79D4	AAT11921.1	<i>Lotus japonicus</i>	TmCYP79E1	AAF66543	<i>Triglochin maritima</i>
MeCYP79D2	AAV97888.1	<i>Manihot esculenta</i>	TmCYP79E2	AAF66544	<i>Triglochin maritima</i>
CYP71 enzymes					
EcCYP706C55	AYN73068	<i>Eucalyptus cladocalyx</i>	PtCYP71B40v3	AIU56748	<i>Populus trichocarpa</i>
FsCYP71AT96	BAU59406	<i>Fallopia sachalinensis</i>	PtCYP71B41v2	AIU56747	<i>Populus trichocarpa</i>
HvCYP71C113	AK250744	<i>Hordeum vulgare L.</i>	PmCYP71AN24	BAP15888.1	<i>Prunus mume</i>
HvCYP71L1	AK248375	<i>Hordeum vulgare L.</i>	SbCYP71E1	AAC39318	<i>Sorghum bicolor</i>
MeCYP71E7	AAP57704.1	<i>Manihot esculenta</i>			
UGT enzymes					
AtUGT76E1	AED97208.1	<i>Arabidopsis thaliana</i>	AtUGT75B1	AEE27854.1	<i>Arabidopsis thaliana</i>
AtUGT76C1	AAP21281.1	<i>Arabidopsis thaliana</i>	AtUGT75B2	AEE27849.1	<i>Arabidopsis thaliana</i>
CrUGT76A2	BAO01108.1	<i>Catharanthus roseus</i>	AtUGT75C1	AAM47973.1	<i>Arabidopsis thaliana</i>
SIUGT76E1	NP001348276.1	<i>Solanum lycopersicum</i>	PfA5GT	Q9ZR27	<i>Perilla frutescens</i>
SrUGT76G1	AAR06912.1	<i>Stevia rebaudiana</i>	RcUGT75L20	AWU66062.1	<i>Rubus chingii</i>
AtUGT85A2	BAA34687	<i>Arabidopsis thaliana</i>	LuUGT85Q1	ADV36300	<i>Linum unsitatissimum</i>
AtUGT85A5	AAF87255	<i>Arabidopsis thaliana</i>	LJUGT85K3	CM0241.610 (gene)	<i>Lotus japonicus</i>
AtUGT85A7	AAF87257	<i>Arabidopsis thaliana</i>	MeUGT85K4	AEO45781.1	<i>Manihot esculenta</i>
AtUGT85A1	AAF18537	<i>Arabidopsis thaliana</i>	MeUGT85K5	AEO45782.1	<i>Manihot esculenta</i>
CrUGT85A23	BAK55749.1	<i>Catharanthus roseus</i>	MtUGT85H2	ABI94024.1	<i>Medicago truncatula</i>
EcUGT85A59	AYN73070.1	<i>Eucalyptus cladocalyx</i>	PIUGT85K31	VVC51334.1	<i>Phaseolus lunatus</i>
GjUGT85A24	BAK55737.1	<i>Gardenia jasminoides</i>	PdUGT85A19	ABV68925.1	<i>Prunus dulcis</i>
GjUGT94E5	BAK55744.1	<i>Gardenia jasminoides</i>	PmUGT85A47	BBE52863.1	<i>Prunus mume</i>
HvUGT85F22	AK252107	<i>Hordeum vulgare L.</i>	SbUGT85B1	AAF17077.1	<i>Sorghum bicolor</i>
HvUGT85F23	AK250769	<i>Hordeum vulgare L.</i>	SrUGT85C2	AAR06916.1	<i>Stevia rebaudiana</i>

Sequence data for all characterized enzymes can be found under the respective Genbank identifier.

Literature:

Bak S, Kahn RA, Nielsen HL, Moller BL, Halkier BA (1998) Cloning of three A-type cytochromes P450, CYP71E1, CYP98, and CYP99 from *Sorghum bicolor* (L.) Moench by a PCR approach and identification by expression in *Escherichia coli* of CYP71E1 as a multifunctional cytochrome P450 in the biosynthesis of the cyanogenic glucoside dhurrin. *Plant Mol Biol* **36**: 393-405

Durst F, Nelson DR (1995) Diversity and Evolution of Plant P450 and P450-Reductases. *Drug Metabolism and Drug Interactions* **12**: 189-206

Gachon CMM, Langlois-Meurinne M, Saindrenan P (2005) Plant secondary metabolism glycosyltransferases: the emerging functional analysis. *Trends in Plant Science* **10**: 542-549

Gotz S, Garcia-Gomez JM, Terol J, Williams TD, Nagaraj SH, Nueda MJ, Robles M, Talon M, Dopazo J, Conesa A (2008) High-throughput functional annotation and data mining with the Blast2GO suite. *Nucleic Acids Res* **36**: 3420-3435

Karabatsos GJ, Hsi N (1967) Structural studies by nuclear magnetic resonance—XI: Conformations and configurations of oxime o-methyl ethers. *Tetrahedron* **23**: 1079-1095

Luck K, Jirschitzka J, Irmisch S, Huber M, Gershenzon J, Kollner TG (2016) CYP79D enzymes contribute to jasmonic acid-induced formation of aldoximes and other nitrogenous volatiles in two *Erythroxylum* species. *BMC Plant Biol* **16**: 215

Pfaffl MW (2001) A new mathematical model for relative quantification in real-time RT-PCR. *Nucleic Acids Res* **29**: e45

Simao FA, Waterhouse RM, Ioannidis P, Kriventseva EV, Zdobnov EM (2015) BUSCO: assessing genome assembly and annotation completeness with single-copy orthologs. *Bioinformatics* **31**: 3210-3212