Pyrrolizidine alkaloid variation in Jacobaea hybrids : influence on resistance against generalist and specialist insect herbivores

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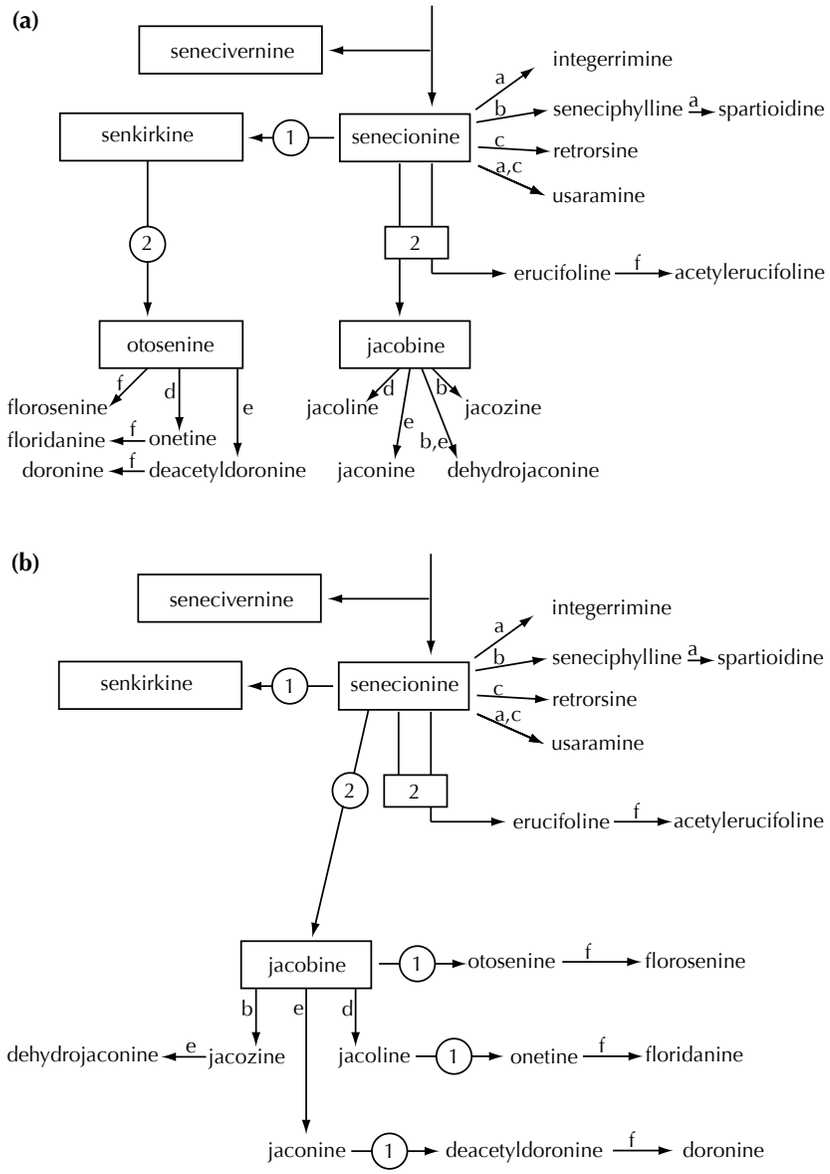
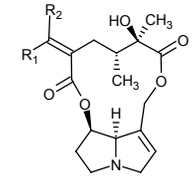
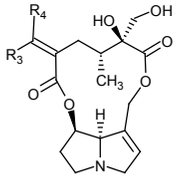


Appendix 1 Putative biosynthetic pathways for diversification of PAs in the *Jacobaea* section.
With the exception of senecivernine, senecionine is the common precursor of all other PAs. Since the substrate specificity of the enzymes involved is not known, two scenarios are illustrated: (a) = senkirkine is assumed to be a common precursor of all otonecine derivatives; (b) = the otonecine derivatives originate independently from the respective retronecine derivatives. Two main reactions exist: conversion of retronecine to otonecine (reaction 1) and site-specific epoxide formation (reaction 2). Further structural diversification requires six simple one-step-reactions marked by letters a–f: a = Z/E-isomerization at C20; b = 13, 19-dehydrogenation; c = site-specific hydroxylations; d = hydrolysis of 15,20-epoxide; e = chlorolysis of 15,20-epoxide; f = site-specific O-acetylations. Adapted from Pelser et al (2005).

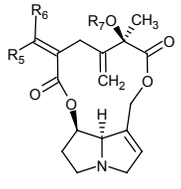
Senecionine - like PAs



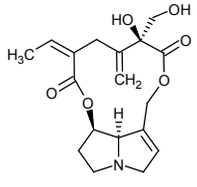
R_1 = CH_3, R_2 = H Senecionine
R_1 = H, R_2 = CH_3 Integerrimine



R_3 = CH_3, R_4 = H Retrorsine
R_3 = H, R_4 = CH_3 Usaramine

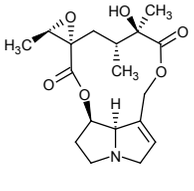


R_5 = CH_3, R_6 = H, R_7 = H Seneciphylline
R_5 = CH_3, R_6 = H, R_7 = Ac Acetylseneciphylline
R_5 = H, R_6 = CH_3, R_7 = H Spartioidine

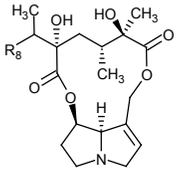


Riddelliine

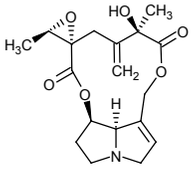
Jacobine - like PAs



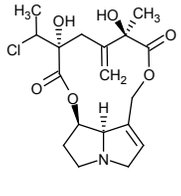
Jacobine



R_8 = OH Jacoline
R_8 = Cl Jaconine

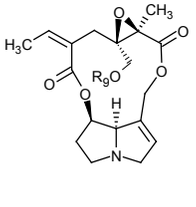


Jacozine



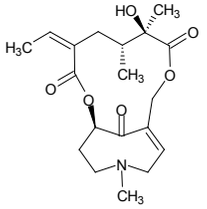
Dehydrojaconine

Erucifoline - like PAs

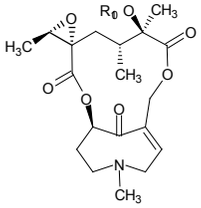


R_9 = H Erucifoline
R_9 = Ac Acetylerucifoline

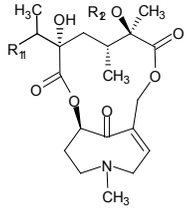
Otosenine - like PAs



Senkirkine



R_{10} = H Otosenine
R_{10} = Ac Florosenine



R_{11} = OH, R_{12} = H Onetine
R_{11} = OH, R_{12} = Ac Floridanine
R_{11} = Cl, R_{12} = H Desacetyldoronine
R_{11} = Cl, R_{12} = Ac Doronine

Appendix 2 Chemical structures of the pyrrolizidine alkaloids (PAs) found in shoots and roots of *J. aquatica*, *J. vulgaris*, F_1 and F_2 hybrids.