



Eckart Eich

Solanaceae and Convolvulaceae: Secondary Metabolites

Biosynthesis, Chemotaxonomy,
Biological and Economic Significance

A Handbook

 Springer

Contents

1	Introduction	1
1.1	Philosophy and Aims of this Book	1
1.1.1	The Large Solanales Families as a Topic	1
1.1.2	General Role of the Secondary Metabolism for a Specific Characterization and Classification of Plant Taxa	1
1.1.3	Bird's-Eye View of Two Centuries of Phytochemical Research on Solanaceae and Convolvulaceae	2
1.2	Secondary Metabolism of the Large Solanales Families	3
1.2.1	Historical Background	3
1.2.2	Common Ground and Differences of the Solanales Families	4
1.2.3	Similar Secondary Metabolism of the Large Solanales Families	5
1.3	Strategy	6
1.4	Criteria for Selection of Secondary Metabolites Based on their Specific Significance	6
1.5	Accumulation or Low-Level Occurrence of Secondary Metabolites	7
1.6	Significance of Chemotaxonomy	8
1.7	Principal Nomenclatural Points	8
1.7.1	Species Names	8
1.7.2	Chemical Trivial Names	8
	References	9
2	Classification and System in Solanales	11
2.1	Position of the Order Solanales and its Families	11
2.1.1	Traditional Systematics	11
2.1.2	Phylogenetic Classification Based on Predominantly (Macro)molecular Data Sets	12

2.2	Solanaceae A.L. DE JUSSIEU: Delimitation, Intrafamilial Circumscription and Relationships	15
2.2.1	Traditional Systematics	15
2.2.2	Phylogenetic Classification Based on Predominantly (Macro)molecular Data Sets	16
2.3	Convolvulaceae A.L. DE JUSSIEU: Delimitation, Intrafamilial Circumscription and Relationships	21
2.3.1	Traditional Systematics	22
2.3.2	Phylogenetic Classification Based on Predominantly (Macro)molecular Data Sets	22
2.4	Uncharted Territory with Regard to Secondary Metabolites of the Solanales	23
	References	28

3 Ornithine-Derived Alkaloids. 33

3.1	Simple Pyrrolidines	65
3.1.1	Discovery and Structural Elucidation	65
3.1.2	Occurrence in the Solanaceae	68
3.1.3	Occurrence in the Convolvulaceae	70
3.1.4	Biosynthesis	73
3.1.5	Significance	74
3.2	N-Acylpyrrolidines (Pyrrolidides, Pyrrolidine Amides)	74
3.2.1	Occurrence in the Solanaceae	75
3.2.2	Occurrence in the Convolvulaceae	75
3.2.3	Biosynthesis	76
3.2.4	Significance	76
3.3	Nicotinoids (Tobacco Alkaloids)	77
3.3.1	Discovery and Structure Elucidation	77
3.3.2	Occurrence in the Solanaceae	87
3.3.3	Occurrence in the Convolvulaceae	94
3.3.4	Biosynthesis of Pyrrolidine-Type Nicotinoids	94
3.3.5	Biosynthesis of Piperidine-/Piperidine-Type Nicotinoids	97
3.3.6	Significance	98
3.4	Tropanes	109
3.4.1	Discovery and Structure Elucidation	109
3.4.2	Occurrence in the Solanaceae	114
3.4.3	Occurrence in the Convolvulaceae	130
3.4.4	Biosynthesis	150
3.4.5	Significance	153
3.5	Calystegines (Polyhydroxylated <i>Nortropans</i>)	160
3.5.1	Discovery and Structure Elucidation	160
3.5.2	Occurrence in the Solanaceae	164

3.5.3	Occurrence in the Convolvulaceae	165
3.5.4	Biosynthesis	175
3.5.5	Significance	176
3.6	<i>Indolizidines</i>	177
3.7	<i>Pyrrolizidines</i>	178
3.7.1	Occurrence in the Convolvulaceae	180
3.7.2	Significance	187
	References	188
4	Tryptophan-derived Alkaloids	213
4.1	β -Carbolines	213
4.1.1	Occurrence in the Solanaceae	213
4.1.2	Occurrence in the Convolvulaceae	214
4.2	Ergolines	215
4.2.1	Discovery and Structure	215
4.2.2	Biosynthesis	218
4.2.3	Occurrence in the Convolvulaceae	222
4.2.4	Location and Origin of Ergoline Alkaloids	241
4.2.5	Significance	245
	References	252
5	Miscellaneous Alkaloids	261
5.1	Occurrence in the Solanaceae	261
5.1.1	Fabianine	261
5.1.2	2-Methoxy-3-isobutylpyrazine	261
5.1.3	Nicotianamine	262
5.1.4	Solamines	263
5.1.5	Pyrrole Alkaloids	263
5.1.6	Benzodiazepines	264
5.1.7	Catecholamines	264
5.1.8	Betaines	264
5.2	Occurrence in the Convolvulaceae	264
5.2.1	Benzyloquinolines	264
5.2.2	Animartinines	266
5.2.3	Lolines	266
5.2.4	Betaines	267
5.2.5	N,N-Diacylspermidines	268
	References	268
6	Phenylalanine-derived Metabolites / Phenylpropanoids	271
6.1	<i>N</i> -Acylphenylethylamines and Derivatives	272
6.1.1	Occurrence in the Solanaceae	272
6.1.2	Occurrence in the Convolvulaceae	272

6.2	Cyanogenic Glycosides	274
6.2.1	Discovery, Distribution in the Plant Kingdom, Ecological Significance	274
6.2.2	<i>Occurrence in the Convolvulaceae</i>	274
6.3	Cinnamate, Hydroxycinnamates and their Derivatives (Phenylpropanoids Sensu Latiore)	275
6.3.1	Phenylpropanoids Sensu Stricto (C ₆ C ₃ Skeleton)	277
6.3.2	Phenylethanoids (C ₆ C ₂ Skeleton)	278
6.3.3	Phenylmethanoids (C ₆ C ₁ Skeleton): Benzoates, Hydroxybenzoates, and their Derivatives	279
6.4	Capsaicinoids	282
6.4.1	Discovery and Structure Elucidation.	282
6.4.2	Botanical Aspects	284
6.4.3	Occurrence.	285
6.4.4	Biosynthesis.	286
6.4.5	Significance	287
6.5	Hydroxycoumarins	292
6.5.1	Occurrence in the Solanaceae	292
6.5.2	<i>Occurrence in the Convolvulaceae</i>	293
6.6	Hydroxycinnamate Conjugates/Caffeic Acid Derivatives	294
6.6.1	Long Chain Alkyl Esters of Hydroxycinnamic Acids	294
6.6.2	Hydroxycinnamoyl Glucose Esters and O-Glucosides	295
6.6.3	Chlorogenic Acid, Dicafeoylquinic Acids, and Related Caffeic Acid Derivatives	295
6.6.4	Hydroxycinnamic Acid Amides	298
6.7	Flavonoids	303
6.7.1	Flavones, Flavonols, and their Derivatives	304
6.7.2	Flavonoid Sulfates	307
6.7.3	Anthocyanins	308
6.7.4	Isoflavonoids	319
6.8	Lignans and Neolignans	321
6.8.1	<i>Occurrence in the Solanaceae</i>	323
6.8.2	<i>Occurrence in the Convolvulaceae</i>	326
	References	329
7	Terpenoids (Isoprenoids)	343
7.1	Hemiterpenoids (C ₅ Isoprenoids)	344
7.1.1	<i>Occurrence in the Convolvulaceae</i>	344
7.2	Monoterpenoids (C ₁₀ Isoprenoids)	345
7.2.1	<i>Occurrence in the Solanaceae</i>	345
7.2.2	<i>Occurrence in the Convolvulaceae</i>	347

7.3	Sesquiterpenoids (C_{15} Isoprenoids)	348
7.3.1	Occurrence in the Solanaceae	348
7.3.2	Occurrence in the Convolvulaceae	356
7.4	Diterpenoids (C_{20} Isoprenoids)	359
7.4.1	Occurrence in the Solanaceae	361
7.4.2	Occurrence in the Convolvulaceae	365
7.5	Triterpenoids (C_{30} Isoprenoids)	366
7.5.1	Occurrence in the Solanaceae	366
7.5.2	Occurrence in the Convolvulaceae	368
7.6	Phytosterols (C_{27} – C_{29} Isoprenoids)	368
7.6.1	Occurrence in the Solanaceae	370
7.6.2	Occurrence in the Convolvulaceae	372
7.7	Steroidal Sapogenins/Saponins (C_{27} Isoprenoids)	372
7.7.1	Discovery and Structure Elucidation	376
7.7.2	Occurrence in the Solanaceae	386
7.7.3	Biosynthesis	393
7.7.4	Significance	395
7.8	Steroidal Alkaloids/Glycoalkaloids (C_{27} Isoprenoids)	399
7.8.1	Discovery and Structure Elucidation	412
7.8.2	Occurrence in the Solanaceae	425
7.8.3	Biosynthesis	441
7.8.4	Significance	447
7.9	Miscellaneous Rare Steroidal Metabolites	460
7.9.1	Homo-cholestane Glycosides (C_{27} + C_2/C_3)	460
7.9.2	Cardenolides	460
7.9.3	Cholecalciferol/Vitamin D_3 and Congeners (C_{27} Isoprenoids)	461
7.9.4	Estrogens (C_{18} Isoprenoids)	464
7.9.5	Ecdysteroids and Antagonists	464
7.9.6	Brassinosteroids (C_{27} + C_1/C_2 Isoprenoids)	465
7.10	Withanolides/Withasteroids (C_{28} Isoprenoids)	466
7.10.1	Discovery	466
7.10.2	Structure	471
7.10.3	Occurrence in the Solanaceae	479
7.10.4	Biosynthesis	480
7.10.5	Significance	480
7.11	Petuniasteroids (C_{28} Isoprenoids)	483
7.11.1	Discovery and Structures	483
7.11.2	Ecological Significance	486
7.12	Tetraterpenoids/Carotenoids (C_{40} Isoprenoids)	486
7.12.1	Solanaceae	487
7.12.2	Convolvulaceae	493
7.12.3	Significance	494
	References	495

8 Secondary Metabolites Derived from Fatty Acids and Carbohydrates	525
8.1 Fatty Acids and Their Derivatives	525
8.1.1 Fatty Acids.....	525
8.1.2 Fatty Acid Amides and Aliphatic Monoamines	527
8.2 Secondary Carbohydrates	529
8.2.1 Occurrence in the Solanaceae	529
8.2.2 Occurrence in the Convolvulaceae	531
8.3 Resin Glycosides (Glycoresins)	532
8.3.1 Discovery and Structural Elucidation	532
8.3.2 Occurrence in the Convolvulaceae	562
8.3.3 Significance.....	564
8.3.4 Convolvulaceous Resin Glycosides versus Solanaceous Steroidal Glycoalkaloids	572
References	573
Appendix: Color Plates of Solanales Species	583
Subject Index	607
Taxonomic Index	625