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ALKALOIDS OF THE SOLANACEAE TRIBE ANTHOCERCIDEAE

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Key Word Index—*Anthocercis*; *Symonanthus*; *Duboisia*; *Cyphanthera*; *Grammosolen*; *Anthotroche*; *Crenidium*; Solanaceae; chemotaxonomy; tropane alkaloids; tobacco alkaloids.

Abstract—All 22 species of the tribe Anthocercideae examined contained tropane alkaloids. *Anthocercis* is characterized by a wide range of alkaloids. The taxonomically reinstated genus *Cyphanthera* shows phytochemical similarities to *Duboisia* in producing tobacco alkaloids (nicotine and anabasine) and tropane esters involving C_3 and C_4 acids. *Anthotroche* species all produce hyoscyamine and accumulate its apo- and nor-derivatives. In accordance with the new taxonomic revision of the tribe, the alkaloid spectra of *Grammosolen* and *Crenidium* resemble those of *Cyphanthera* species.

INTRODUCTION

In a recent conspectus of Solanaceae tribe Anthocercideae Haegi [1] recognises the seven genera *Anthocercis*, *Symonanthus*, *Duboisia*, *Cyphanthera*, *Grammosolen*, *Anthotroche* and *Crenidium*. *Grammosolen* Haegi and *Crenidium* Haegi are newly described genera and *Symonanthus* Haegi is provided to replace *Isandra* F. Muell.; *Anthocercis* Labill. and *Anthotroche* Endl. are redefined, *Cyphanthera* Miers is reinstated and *Duboisia* R.Br. remains unchanged. The twenty-nine species involved are described and arranged in accordance with the revised taxonomy in the *Flora of Australia* [2].

The known occurrence of tropane and tobacco alkaloids in some members of the tribe suggested that a systematic phytochemical study, carried out in relation to the new taxonomic divisions, could prove of chemotaxonomic significance. Tropane alkaloids have been reported previously in *Anthocercis littorea* [3, 4], *A. fasciculata* [3], *A. viscosa* [3, 4], *Cyphanthera anthocercidea* (*A. frondosa*) [5], *C. albicans* (*A. albicans*) [6], *C. tasmanica* (*A. tasmanica*) [7], *Anthotroche pannosa* [6, 8], *A. myoporoides* [6], and *A. walcottii* [6]. The tropane alkaloids of *Duboisia* are well documented [9]; nicotine occurs in *Cyphanthera tasmanica* [7] and in *Duboisia* species [9].

We report here the results of the phytochemical examination of plant material collected by Mr. L. Haegi during expeditions in connection with the taxonomic revision of the tribe; some samples analysed constitute type collections of new taxa now described in the *Flora of Australia* [2].

RESULTS AND DISCUSSION

The alkaloid spectra of 22 species and four subspecies of the Anthocercideae are given in Table 1. The specific identities of the alkaloids involved in columns C, D and E of the Table, and the extent to which it has been possible to identify individual alkaloids, are given in the Experimental Section.

Tropane alkaloids, albeit often in low concentration, appear to be an overall characteristic of the tribe; hyoscyamine and hyoscine or their derivatives are usually, although not invariably, the major alkaloids. With the exception of the dimeric bases of *Schizanthus* [10] and *Atropa* (belladonnine) all major classes of tropane alkaloid found elsewhere in the Solanaceae [9] are represented in the tribe.

Anthocercis species contain either hyoscyamine or hyoscine as predominant alkaloids frequently accompanied by their respective apo- and nor-derivatives. Considerable intra-specific variation in total alkaloid content is evident; thus one collection of *A. genistoides* was almost devoid of alkaloid whereas the roots of another contained 0.15 per cent total alkaloids and afforded the new alkaloid aponorhyoscine [6]. Littorine, the 2-hydroxy-3-phenylpropionic acid ester of tropine, appears to be confined to this genus. The probable existence of a new alkaloid, acetoxyhyoscyamine, in *A. angustifolia* deserves further investigation. Bulk samples of both *A. littoria* and *A. viscosa* have previously been analysed [3] in some detail; the further results now obtained indicate little difference in alkaloid content between *A. littoria* and the very closely related *A. ilicifolia*, and little difference between varieties of *A. viscosa*. Esters of tiglic acid are common in *Anthocercis* but those of the saturated C_4 and C_5 acids are lacking, cf. *Cyphanthera* and *Duboisia* below.

The new genus *Symonanthus* Haegi (2 spp.) [1] is regarded as most closely related to *Anthocercis*; the species, *S. aromaticus* (*Anthocercis aromaticus* C. A. Gardner), examined chemically was unique in containing in both roots and aerial parts derivatives of hyoscine and tiglic acid only, the latter forming the principal alkaloidal components of the roots. An investigation of other collections of this species would be useful.

Haegi [1] has reinstated the genus *Cyphanthera* Miers (9 spp.), it having been previously reduced to a section of *Anthocercis sensu lat.* by Bentham in 1868, a situation which took no account of the close affinity of the former to *Duboisia*. Phytochemically the distinction of the genus from *Anthocercis* and the affinity with *Duboisia* is most marked. Thus in common with *Duboisia* three of the eight

Table 1. Alkaloids of the tribe Anthocercideae

	Total tropic and atropic acid esters. % Dry wt	Alkaloids identified* A	B	C	D	E	Others
Genus *Anthocercis* Labill.							
A. angustifolia. Aerial parts	0.11	++	+	—	+	+	?6-Acetoxyhyoscyamine 6β-Acetoxy-3α-tigloyloxytropane
A. anisantha ssp. *anisantha* (Voucher, Haegi 1090). Aerial parts	0.02	++	+	+	+	+	Littorine
A. anisantha ssp. *anisantha* (Voucher, Haegi 1296)		++	+	+	+	—	
A. anisantha ssp. *collina.* Aerial parts		++	+	+	+	—	
A. genistoides (Voucher, Haegi, 1019) Aerial parts	< 0.01						
A. genistoides (Voucher, Haegi 958)	0.04	++	—	+	—	+	
A. genistoides (Voucher, Haegi 1036) Aerial parts	0.03	+	++	+	—	—	
Roots	0.15	+	++	+	+	+	Aponorhyoscine ?Hydroxyhyoscyamine
A. genistoides (Voucher, Haegi 1783) Aerial parts†	0.08 (total alkaloids by titration)	+	+	+	—	++	?Hydroxyhyoscyamine Tropine
A. gracilis. Aerial parts	0.03	+	++	—	+	—	
A. ilicifolia ssp. *ilicifolia* Aerial parts†	0.25 (total alkaloids by titration	—	++	+	+	+	Littorine 6-Hydroxyhyoscyamine, Tropine
Roots†	0.23 (total alkaloids by titration)	+	++	+	+	+	Littorine 6-Hydroxyhyoscyamine, Tropine
A. intricata. Aerial parts	0.08	++	+	+	—	+	6β-Acetoxy-3α-tigloyloxytropane
A. littorea. Aerial parts	0.03	++‡	+	+	+	+	Littorine, Tropine
A. viscosa ssp. *viscosa* Aerial parts†	0.02 (total alkaloids	++	+	—	+	+	Two unidentified bases
Roots†	0.02 by titration)	++	—	—	+	+	
A. viscosa ssp. *caudata* Aerial parts	0.04	++	+	+	+	+	Tropine
Root-bark	0.02	+	—	—	+	+	
Genus *Symonanthus* Haegi							
S. aromaticus							
Aerial parts	0.01	—	+	—	+	+	
Root-bark	0.03	—	+	—	+	++	
Genus *Duboisia* R.Br. see text							
Genus *Cyphanthera* Miers							
C. albicans ssp. *albicans* Aerial parts	0.05	+	+	—	+	+	3α-Isobutyryloxytropan-6β-ol, 3α-Acetoxytropane, Valeroidine 3α-Isobutyryloxytropane, Valtropine
Roots	0.05	+	+	—	+	+	3α-Acetoxytropane 3α-Isobutyryloxytropane, Valtropine, 6-Hydroxyhyoscyamine
C. albicans ssp. *notabilis* Stem-bark	0.01	+	++	—	+	—	Tropine
Leaves	0.02	—	++	—	+	+	3α-(*n*-Butyryloxy)tropane, 3α-Acetoxytropane, Unidentified base

Roots	0.07	—	++	—	+	—	Unidentified base
C. anthocercidea Stem-bark	0.025	+	++	—	+	—	Nicotine, Tropine, Unidentified base
Leaves	0.21	+	+	+	—	—	Nicotine (major alkaloid), Anabasine, Nornicotine, Tropine
Roots	0.07	+	++	—	+	—	Nicotine, *Unidentified pyridine derivative*
C. microphylla Aerial parts	< 0.01	+	—	—	+	—	Unidentified bases
C. myosotidea Aerial parts†	0.11 (total alkaloids by titration)	+	++	+	+	+	6-Hydroxyhyoscyamine, ? 6,7-Dihydroxy-3-phenylacetoxynortropane, Scopine
C. odgersii ssp. *odgersii* Aerial parts†	0.08 (total alkaloids by titration)	+	++	+	+	—	6-Hydroxyhyoscyamine, Tropine
C. odgersii ssp. *occidentalis* Aerial parts	0.10	+	++	—	+	—	6-Hydroxyhyoscyamine, Tetramethylputrescine
C. racemosa Aerial parts	0.01						Nornicotine, Anabasine Unidentified base
Roots	No alkaloids detected						
C. scabrella Aerial parts	0.06	?+	++	—	+	—	? Valeroidine
C. tasmanica Aerial parts†	0.17 (total alkaloids by titration)	+	+	—	—	?+	Nicotine (principal alkaloid), Tropine
Root-bark†	0.16 (total alkaloids by titration)	+	+	—	+	—	Nicotine (principal alkaloid), Tropine, ? Valeroidine
Genus *Grammosolen* Haegi							
G. dixonii Aerial parts	0.004	+	+	—	+	—	3α-Acetoxytropane
Roots	0.03	?+	+	—	+	—	Valtropine, 6-Hydroxyhyoscyamine
Genus *Anthotroche* Endl.							
A. myoporoides Aerial parts	0.04	+	+	++	+	—	Aponoratropine
Roots	0.02	+	—	+	—	—	Tropine (major alkaloid), 3α-Acetoxytropane
A. pannosa complex (Voucher, Haegi 1131)							
Aerial parts	0.01	++	+	+	+	—	Tropine
Roots	0.02	++	—	+	—	—	Tropine
A. pannosa complex (Voucher, Haegi 1165)							
Aerial parts	0.01	++	+	+	+	—	
A. walcottii. Aerial parts	0.02	++	+	+	+	—	Aponoratropine
Roots	0.04	+	—	++	—	—	
Genus *Crenidium* Haegi							
C. spinescens Aerial parts†	0.09 (total alkaloids by titration)	++	+	+	+	—	Tropine, 6-Hydroxyhyoscyamine, Anabasine
Roots†	0.21 (total alkaloids by titration)	++	+	+	+	—	6-Hydroxyhyoscyamine

*A = hyoscyamine; B = hyoscine; C = nor-derivatives; D = apo-derivatives; E = tigloyl esters.

+ = Alkaloid identified by characters listed in "Experimental". ++ = Principal component of basic mixture.

†Results made available prior to full publication, see [13].

‡Atropine

species examined contained nicotine derivatives and two of them anabasine as well; three species from which tobacco alkaloids were not isolated produced esters involving saturated four- or five-carbon acids. Tetramethylputrescine, a component of *Duboisia myoporoides* [10] was isolated from *Cyphanthera odgersii* subsp. *occidentalis*. On the other hand tigloyl esters, a universal feature of *Anthocercis* are either absent from, or exhibit a limited structure range in, *Cyphanthera* species.

Grammosolen Haegi (2 spp.) is most closely related to *Cyphanthera* and *Anthotroche* [1]; the alkaloid spectrum of *Grammosolen dixonii* (formerly *Newcastelia dixonii*, family Verbenaceae) resembles that of the nicotine-free species of *Cyphanthera*. One feature of the alkaloid mixture of the three species of *Anthotroche* is the predominance of hyoscyamine or norhyoscyamine; apoderivatives are also present so that the isolation of the new natural alkaloid, aponoratropine, from two species [6], was not unexpected. The new genus *Crenidium* Haegi [1] consists of the single species *C. spinescens* Haegi; hyoscyamine is the predominant alkaloid and anabasine (*cf. Cyphanthera*) occurs in the leaves.

Overall the distribution pattern of alkaloids within species and genera is consistent with Haegi's [1] recent taxonomic division of the Anthocercideae into those genera having bilocular anthers (*Anthocercis, Symonanthus*) and those with unilocular anthers (*Duboisia, Cyphanthera, Grammosolen, Anthotroche* and *Crenidium*). The alkaloid components of the various species of a genus are generally consistent but alkaloid characteristics alone would not always suffice to delineate a genus. As the relative proportions of different alkaloids in *Duboisia myoporoides* are known [12] to vary with climate and genetical constitution further studies on some of the species analysed here would not be inappropriate.

EXPERIMENTAL

Plant materials. Collection details and herbarium depositions for the species examined are given in Table 2.

Table 2. Plant materials

Species	Habitat and Australian locality	Date collected	Collector and No.	Herbarium deposition
Anthocercis angustifolia F. Muell.	Slender shrub, 1–1.5 m. Western scarp of Mt. Lofty Range, E. of Adelaide.	Sept. 1975	Symon 10393	AD
A. anisantha Endl. ssp. *anisantha*	Mature shrub, 2.3 m. *ca* 10 km N of Merredin, W. A.	Sept. 1976	Haegi 1090	AD
A. anisantha Endl. ssp. *anisantha*	Mature shrub, 1.2 m. Cape Donington, Pt. Lincoln, S.A.	Aug. 1977	Haegi 1296	NSW
A. anisantha Endl. ssp. *collina* Haegi	Mature shrub, 0.7 m. Carappee Hill, *ca* 35 km SSW of Kimba, S.A.	Aug. 1977	Haegi 1311	NSW
A. genistoides Miers	Mature shrub, 1.7 m. *ca* 20 km SSE of Ravensthorpe, W.A.	Sept. 1976	Haegi 1019	AD
A. genistoides Miers	Mature shrub, 1.0 m. Peak Charles, *ca* 130 km NW Esperance, W.A.	Sept. 1976	Haegi 958	AD
A. genistoides Miers	Mature shrub 1.3 m. 15 km SW of Ravensthorpe, W.A.	Sept. 1976	Haegi 1036	AD
A. genistoides Miers	Mature shrub 2.0 m. Moorine Rock, W.A.	Aug. 1979	Haegi 1783	NSW
A. gracilis Benth.	Mature undershrub 0.5 m. *ca* 22 km ESE of Perth, W.A.	Oct. 1976	Haegi 1161	AD
A. ilicifolia Hook. ssp. *ilicifolia*	Mature shrub 2.5 m. *ca* 20 km SSE of Lancelin, W.A.	Aug. 1979	Haegi 1894	NSW
A. intricata F. Muell.	Mature shrub 3.0 m. *ca* 5.0 km SSE of Geraldton, W. A.	Sept. 1976	Haegi 1160	AD
A. littorea Labill.	Mature shrub 1.0 m. *ca* 12 km SSE of Albany, W.A.	Sept. 1976	Haegi 1052	AD
A. viscosa R.Br. ssp. *viscosa*	Mature shrub 2.3 m. Mount Clarence, Albany, W.A.	Sept. 1976	Haegi 1049	AD
A. viscosa R.Br. ssp. *caudata* Haegi	Mature shrub 1.7 m. *ca* 62 km ENE of Esperance, W.A.	Oct. 1976	Haegi 1225 (type collection)	AD
Symonanthus aromaticus (C. A. Gardner) Haegi	Mature shrub 1.0 m. *ca* 13 km NW of Newdegate, W.A.	Sept. 1976	Haegi 1072	AD
Cyphanthera albicans (A. Cunn.) Miers ssp. *albicans*	Mature shrub 1.5 m. *ca* 45 km NE of Hillston, N.S.W.	Sept. 1977	Haegi 1363	NSW
C. albicans A. Cunn ssp. *notabilis* Haegi	Mature shrub 1.8 m. *ca* 10 km W of Coomabarabran, N.S.W.	Sept. 1977	Haegi 1379 (type collection)	NSW
C. anthocercidea (F. Muell.) Haegi [*Anthocercis frondosa* (Miers) J. M. Black]	Mature shrub 2 m. Mt. Zero, *ca* 25 km SE of Horsham, Vic.	Sept. 1977	Haegi 1450	NSW
C. microphylla F. Muell.	Mature undershrub 0.3 m.	Sept. 1976	Haegi 983	AD

Table 2. (*Contd.*)

Species	Habitat and Australian locality	Date collected	Collector and No.	Herbarium deposition
	ca 70 km ENE of Lake King, W.A.			
C. myosotidea F. Muell.	Mature undershrubs 0.1–0.2 m. *ca* 20 km NE of Blanchetown on Waikerie road, S.A.	Sept. 1978	Haegi 1592	NSW
C. odgersii (F. Muell.) ssp. *odgersii* Haegi	Mature shrub 0.5 m. *ca* 90 km SW of Coolgardie, W.A.	Aug. 1979	Haegi 1780	NSW
C. odgersii (F. Muell.) ssp. *occidentalis* Haegi	Mature shrub 1.4 m. *ca* 90 km NW of Merredin, W.A.	Sept. 1976	Haegi 1100 (type collection)	AD
C. racemosa (F. Muell.) Haegi	Mature shrub 1 m. *ca* 60 km SE of Geraldton, W.A.	Sept. 1976	Haegi 1144	AD
C. scabrella (Benth.) Miers	Mature shrub 1 m. Bowers Creek *ca* 85 km NW of Sydney, N.S.W.	Sept. 1977	Haegi 1417	NSW
C. tasmanica Miers	Pot-grown at Waite Institute, Glen Osmond from cuttings collected in Tasmania by Mr. Himson	May 1980	Himson 51139–51141	ADW
Grammosolen dixonii (F. Muell. & R. Tate) Haegi	Mature shrub *ca* 20 km NE of Blanchetown on Waikere road, S.A.	Aug. 1976	Symon 10595	ADW
Anthotroche myoporoides C. A. Gardn.	Mature shrub 2 m. *ca* 70 km NE of Geraldton, W.A.	Sept. 1976	Haegi 1156	AD
A. pannosa Endl. complex	Mature shrub 1.5 m. *ca* 140 km SE of Geraldton, W.A.	Sept. 1976	Haegi 1131	AD
A. pannosa Endl. complex	Mature shrub 1.5 m. On Great Eastern Hwy., 18 km WNW of Cunderdin, W.A.	Oct. 1976	Haegi 1165	AD
A. walcottii F. Muell.	Mature shrub 1.0 m. *ca* 100 km NW of Geraldton, on Kalbarri road, W.A.	Sept. 1976	Haegi 1153	AD
Crenidium spinescens Haegi	Mature shrub, not flowering. Very dry season. Lake Goongarrie, *ca* 90 km N of Kalgoorlie, W.A.	Aug. 1977	Pearce 110	ADW

Extraction and fractionation of alkaloids. The extraction, fractionation and determination of alkaloids followed in general the methods previously described [4]. Thus alkaloids were extracted from the moistened, basified $Ca(OH)_2$, plant material with Et_2O and purified by the Stas–Otto procedure. Fractionation of the alkaloid mixture was achieved by column chromatography, TLC and PLC. Total bases in the plant extract were determined by titration and tropoyl esters by a modified Vitali–Morin reaction.

Characterization of alkaloids. The structural determination of a number of new alkaloids isolated in this study has already been reported [6]. Known alkaloids were identified by comparison with authentic samples using R_f values in one to four systems, the mp and mmp of picrates, and IR, NMR and MS. Where appropriate, high resolution and chemical ionization MS were utilized. The specific alkaloids isolated from each sample and the extent to which their characterization was possible, depending on sample size, alkaloid content and purity of the isolated alkaloid, are given below.

Anthocercis angustifolia. Leaves 75.0 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); hyoscine (TLC, mp and mmp of picrate, IR, MS); 6β-acetoxyhyoscyamine in admixture with hyoscine (TLC, MS of mixture and acetylated mixture compared with that of reference acetylated mixture); apoatropine (TLC, IR, MS); apohyoscine and 3α,6β-ditigloyloxytropane in admixture (TLC—3 systems, MS); 6β-acetoxy-3α-tigloyloxytropane (TLC—3 systems, mp and mmp of picrate, IR, MS); tigloidine (TLC—3 systems, MS); 6β-tigloyloxytropan-3α-ol (TLC—2 systems, MS).

Anthocercis anisantha *subsp.* anisantha (*Voucher: Haegi* 1090). Aerial parts 260 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); hyoscine (TLC, mp and mmp of picrate, IR, MS); littorine (TLC—3 systems, IR, MS); norhyoscyamine (TLC—3 systems); apoatropine (TLC—2 systems, MS); apohyoscine and 3α,6β-ditigloyloxytropane in admixture (TLC—3 systems, MS); 3α,6β-ditigloyloxytropan-7β-ol (TLC, mp and mmp of picrate, IR, MS).

Anthocercis anisantha *subsp.* anisantha (*Voucher: Haegi* 1296). Leaves 20 g. Hyoscyamine, (TLC, mp and mmp of picrate); hyoscine (TLC—2 systems, MS); norhyoscyamine (TLC, mp and mmp of picrate); apoatropine (TLC—4 systems).

Anthocercis anisantha *subsp.* collina. Leaves 14 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); hyoscine (TLC—2 systems, MS); norhyoscyamine (TLC, mp and mmp of picrate, IR, MS); apoatropine (TLC—4 systems).

Anthocercis genistoides (*Voucher: Haegi* 1019). Leaves 20 g. Alkaloid content (Vitali–Morin assay) 0.006%. No alkaloids identified in the concentrated extract of the leaf material.

Anthocercis genistoides (*Voucher: Haegi* 958). Aerial parts 26 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); norhyoscyamine (TLC, mp and mmp of picrate, IR, MS); meteloidine in admixture with hyoscyamine (TLC—3 systems, MS of mixed bases).

Anthocercis genistoides (*Voucher: Haegi* 1036). Leaves 90 g. Hyoscyamine (tentative identification by TLC—3 systems); hyoscine (TLC, mp and mmp of picrate, IR, MS); norhyoscine (TLC, mp and mmp, IR, MS); apohyoscine (TLC, IR, MS). Roots 11 g. Hyoscyamine and meteloidine in admixture (TLC—3 systems, MS of mixture); hyoscine (TLC, mp and mmp of picrate, IR, MS); norhyoscine (TLC, mp and mmp of picrate, IR); 6β-

hydroxyhyoscyamine in admixture with other bases (tentative identification by TLC, MS); apohyoscine (TLC, IR, MS); 3α,6β-ditigloyloxytropane and 3α,6β-ditigloyloxytropan-7β-ol in admixture (tentative identification by TLC and MS); aponorhyoscine, see [6]; other bases (MS).

Anthocercis genistoides (*Voucher: Haegi* 1783). Meteloidine the principal alkaloid, see [13].

Anthocercis gracilis. Aerial parts 27 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); hyoscine (TLC, mp and mmp of picrate, IR, MS); apoatropine (tentative identification by TLC—3 systems); other bases (TLC).

Anthocercis ilicifolia *subsp.* ilicifolia. See [13].

Anthocercis intricata. Aerial parts 65 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); hyoscine (TLC, mp and mmp of picrate, IR, MS); norhyoscyamine (TLC, mp and mmp of picrate, IR, MS); 6β-acetoxy-3α-tigloyloxytropane (TLC, mp and mmp of picrate, IR, MS); 3α-tigloyloxytropan-6β-ol and meteloidine in admixture (TLC—3 systems, MS of mixture).

Anthocercis littorea. Aerial parts 155 g. Atropine (TLC, mp and mmp of picrate, IR, MS); hyoscine in admixture with other bases (tentative identification by TLC and MS); norhyoscyamine (TLC, IR, MS); apoatropine (TLC—3 systems, MS); littorine (TLC, IR, MS); tigloidine (TLC—3 systems, MS); 3α,6β-ditigloyloxytropan-7β-ol (TLC, MS); 3α,6β-ditigloyloxytropane (TLC, mp of picrate, IR, MS); meteloidine (TLC, mp and mmp of the picrate, IR, MS); tropine (TLC, mp of picrate, IR, MS).

Anthocercis viscosa *subsp.* caudata. Aerial parts 115 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); hyoscine (TLC, IR, MS); norhyoscyamine (TLC, mp, IR, MS); apoatropine (TLC—4 systems); apohyoscine and 3α,6β-ditigloyloxytropane in admixture (TLC—4 systems); 3α,6β-ditigloyloxytropan-7β-ol (TLC—4 systems, MS); 3α-tigloyloxytropane (TLC—3 systems, MS), meteloidine (TLC—3 systems); tropine (TLC—3 systems). Root-bark 33 g. Hyoscyamine (tentative identification by TLC—3 systems); apoatropine (TLC—3 systems, MS); 3α,6β-ditigloyloxytropane (TLC, MS); 3α,6β-ditigloyloxytropan-7β-ol (TLC, IR, MS).

Symonanthus aromaticus. Aerial parts 210 g. Hyoscine (TLC, mp, IR, MS); apohyoscine (TLC, mp, IR, MS); 3α-tigloyloxytropan-6β-ol (TLC—2 systems, MS); other minor bases (TLC). Root-bark 68 g. Hyoscine (TLC, mp and mmp of picrate, IR, MS); apohyoscine and 3α,6β-ditigloyloxytropane in admixture (TLC—3 systems, MS); 3α,6β-ditigloyloxytropan-7β-ol (TLC, MS); tigloidine (TLC—2 systems, MS); 3α-tigloyloxytropane (TLC—3 systems, MS); 6β-tigloyloxytropan-3α-ol (TLC—2 systems, MS); 3α-tigloyloxytropan-6β-ol (TLC—2 systems, MS); other bases (TLC).

Cyphanthera albicans *subsp.* albicans. Aerial parts 250 g. Hyoscine (TLC, mp and mmp of picrate, IR, MS); hyoscyamine (TLC—4 systems); apohyoscine and 3α,6β-ditigloyloxytropane in admixture (TLC—4 systems); 3α-tigloyloxytropane (TLC—4 systems); 3α-acetoxytropane (TLC—4 systems); valeroidine (TLC, MS); 3α-isobutyryloxytropane (TLC, IR, MS); valtropine in admixture with 3α-isobutyryloxytropane (tentative identification by MS); 3α-isobutyryloxytropan-6β-ol (for structure determination see [6]). Roots 70 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); hyoscine (TLC, mp and mmp of picrate, IR, MS); apohyoscine (TLC, MS); apoatropine in admixture with hyoscyamine (TLC—3 systems, MS); 6β-hydroxyhyoscyamine (TLC—2 systems, MS); 3α-tigloyloxytropan-6β-ol (TLC—3 systems); 3α-acetoxytropane (TLC, IR, MS); 3α-isobutyryloxytropane (TLC, mp and mmp of picrate, IR, MS); valtropine in admixture with 3α-isobutyryloxytropane (tentative identification by TLC, IR, MS).

Cyphanthera albicans *subsp.* notabilis. Stem-bark 129 g. Hyoscyamine (TLC—3 systems); hyoscine (TLC, mp and mmp of picrate, IR, MS); apohyoscine (TLC—4 systems); tropine (TLC—3 systems). Leaves 264 g. Hyoscine (TLC, mp and mmp of picrate, IR, MS); apohyoscine (TLC, mp and mmp of picrate, IR, MS); apoatropine (tentative identification by TLC—3 systems); 3α-tigloyloxytropane (tentative identification by TLC—3 systems); 3α-acetoxytropane (TLC, IR, MS); 3α-(*n*-butyryloxy)tropane (for structure elucidation see [6]). Roots 19 g. Hyoscine (TLC, mp and mmp of picrate, IR, MS); apohyoscine (TLC—3 systems); unidentified base (TLC).

Cyphanthera anthocercidea. Stem-bark 145 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); hyoscine (TLC, mp and mmp of picrate, IR, MS); apohyoscine (TLC, mp and mmp of picrate, IR, MS); apoatropine (TLC—4 systems); tropine (TLC—3 systems); nicotine (TLC, mp and mmp of dipicrate, IR, MS); unidentified base (TLC, IR, MS). Leaves 150 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); hyoscine (TLC, mp and mmp of picrate, IR, MS); norhyoscyamine (TLC, mp, IR, MS); tropine (TLC—3 systems); nicotine (TLC, mp and elemental analysis of dipicrate, IR, NMR, MS); nornicotine (TLC—2 systems, IR, MS); anabasine (TLC—2 systems, IR, MS). Roots 62 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); hyoscine (TLC, mp and mmp of picrate, IR, MS); apohyoscine (TLC, IR, MS); apoatropine (TLC—4 systems); nicotine (TLC, mp and mmp of dipicrate, IR, MS); unidentified pyridine derivative (TLC, MS).

Cyphanthera microphylla. Aerial parts 98 g. Hyoscyamine (tentative identification by TLC—4 systems); apohyoscine (tentative identification by TLC—4 systems); unidentified base (TLC).

Cyphanthera myosotidea. See [13].

Cyphanthera odgersii *subsp.* odgersii. See [13].

Cyphanthera odgersii *subsp.* occidentalis. Aerial parts 250 g. Hyoscyamine (TLC, mp of picrate, IR, MS); hyoscine (TLC, mp and mmp of picrate, IR, MS); 6-hydroxyhyoscyamine (TLC, MS); tetramethylputrescine (TLC—2 systems, MS); apohyoscine (TLC, mp of picrate, IR, MS).

Cyphanthera racemosa. Aerial parts 206 g. Nornicotine (TLC, mp, IR, MS); anabasine (TLC, mp, IR, MS); unidentified base (picrate mp 170–172°; IR gave ester carbonyl at 1710 cm^{-1}, MS indicated neither a tropane nor a pyridine alkaloid).

Cyphanthera scabrella. Aerial parts 38 g. Hyoscyamine and valeroidine in admixture (tentative identification by TLC and MS); hyoscine (TLC, mp and mmp of picrate, IR, MS); apohyoscine (TLC, mp and mmp of picrate, IR, MS).

Cyphanthera tasmanica. See [13].

Grammosolen dixonii. Aerial parts 245 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); hyoscine (TLC, mp and mmp of picrate, IR, MS); apohyoscine and 3α-acetoxytropane in admixture (TLC, MS). Roots 70 g. Hyoscyamine (tentative identification by TLC—3 systems); hyoscine (TLC, MS), apoatropine and valtropine in admixture (TLC, MS); 6β-hydroxyhyoscyamine (TLC, MS); other bases (TLC).

Anthotroche myoporoides. Aerial parts 200 g. Hyoscyamine (TLC, IR, MS); hyoscine (TLC, mp, IR, MS); norhyoscyamine (TLC, mp and mmp of picrate, IR, MS); apoatropine in admixture with other bases (TLC, MS); aponoratropine, see [6] for structural elucidation. Roots 146 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); norhyoscyamine (TLC, mp and mmp of picrate, IR, MS); 3α-acetoxytropane (TLC, IR, MS); tropine (TLC, mp of picrate, IR, MS).

Anthotroche pannosa *complex* (*Voucher: Haegi* 1131). Aerial parts 190 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); hyoscine (TLC, IR, MS); apoatropine (TLC, IR, MS); norhyoscyamine (TLC, mp and mmp of picrate, IR, MS); tropine (TLC—3 systems). Roots 11 g. Hyoscyamine (TLC, mp of picrate, IR, MS); norhyoscyamine (TLC—3 systems), tropine

(TLC—3 systems).

Anthotroche pannosa *complex* (*Voucher: Haegi* 1165). Aerial parts 96 g. As previous sample, but tropine not detected.

Anthotroche walcottii. Aerial parts 190 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); hyoscine (tentative identification by TLC and MS); apoatropine (TLC—3 systems, MS); aponoratropine, see [5] for structural determination; norhyoscyamine (TLC, mp and mmp of picrate, IR, MS). Roots 30 g. Hyoscyamine (TLC, mp and mmp of picrate, IR, MS); norhyoscyamine (TLC, mp and mmp of picrate, IR, MS).

Crenidium spinescens. See [13].

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