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Revisión | Review

Alkaloids from the native flora of Chile: a review

[Alcaloides de la flora nativa de Chile: una revisión]

Javier ECHEVERRÍA & Hermann M. NIEMEYER

Departamento de Ciencias Ecológicas, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile
Contactos | Contacts: Javier Echeverría - E-mail address: javier.echeverriam@usach.cl
Contactos | Contacts: Hermann M. Niemeyer - E-mail address: niemeyer@abulafia.ciencias.uchile.cl

Abstract:
In spite of the high degree of endemism of the native vascular flora of Chile (*ca*. 52%) and predictions based on the frequency of occurrence of alkaloids in the world flora (they have been found in 40.4% of the families, 13.1% of the genera and 2.7% of the species), alkaloids have been isolated from only 12.5% of families, 3.9% of genera and 1.7% of species of the native flora of Chile. The slope of the linear correlation between these two sets of figures suggests that the alkaloid potential of the native Chilean flora has been exploited to the extent of only 29%. Currently known alkaloid-containing species from the native flora of Chile are listed in this review together with pertinent references. The distribution of alkaloids was compared between the native flora of Chile and the world flora; this led to the identification of several families with good potential as sources of alkaloids.

Keywords: Alkaloids; native flora of Chile; potential sources of alkaloids; alkaloid distribution in floras; alkaloid distribution in ecosystems

Resumen:
A pesar del alto grado de endemismo de la flora vascular nativa de Chile (*ca*. 52%) y predicciones basadas en la frecuencia con que se encuentran alcaloides en la flora del mundo (en 40.4% de las familias, 13.1% de los géneros y 2.7% de las especies), se han aislado alcaloides solo desde 12,5% de las familias, 3,9% de los géneros y 1,7% de las especies de la flora nativa de Chile. La pendiente de la correlación entre estos dos conjuntos de datos sugiere que el potencial de la flora nativa de Chile como productora de alcaloides ha sido explotado solo en un 29%. En esta revisión se entrega una lista de las especies de la flora nativa de Chile que contienen alcaloides y las referencias pertinentes. La distribución de alcaloides fue comparada entre la flora nativa de Chile y la flora del mundo, lográndose identificar varias familias con un buen potencial como fuentes de alcaloides.

Palabras Clave: Alcaloides; flora nativa de Chile; fuentes potenciales de alcaloides; distribución de alcaloides en floras; distribución de alcaloides en ecosistemas

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INTRODUCTION

The continental territory of Chile is a long (18º to 56ºS) and narrow stretch of land lying between the Andes range and the Pacific Ocean. Within this area, vegetational zones may be distinguished which encompass one of the driest deserts on earth, the Atacama desert, and cool temperate rain forests with average annual rainfall in excess of 4.5 m (Gajardo, 1994). The geographical isolation of the country as well as the variety of vegetational zones given by its latitudinal and altitudinal expanses has produced a unique land flora with a notably high degree of endemism (51.8%) in relation to its relatively meager surface area (Major, 1988). This flora comprises 184 families of vascular plants (18 Pteridophyta, 4 Gymnospermae, 132 Dicotyledoneae and 30 Monocotyledoneae) subdivided into 1008 genera, with a total of 5739 species, including 5082 native species of which 2630 are endemic (Marticorena, 1990). The uniqueness of the Chilean flora is also exceptional, with 496 monotypic genera, some families with higher than 80% endemism (i.e., Cactaceae) and some genera with higher than 70% endemism [*i.e.*, *Neoporteria* (Cactaceae), *Cristaria* (Malvaceae) and *Haplopappus* (Asteraceae)] (Niemeyer 1995).

Alkaloids are widespread in Nature; they show a wide range of pharmacological activities and many of them are used as drugs (Cordell *et al*., 2001). In spite of the uniqueness of the native flora of Chile, predictions based on the frequency of occurrence of alkaloids in the world flora, and their interesting pharmacological activities, studies on alkaloids from the native Chilean flora have been rather scarce. This review gathers information on the alkaloid-containing taxa of the native Chilean flora and compares it with data for the world flora.

RESULTS AND DISCUSSION

Table 1 lists the alkaloid-containing taxa from the native Chilean flora. The data for Loranthaceae and Cuscutaceae deserve a special comment. *Tristerix verticillatus* (Loranthaceae) and *Cuscuta chilensis* (Cuscutaceae) are hemiparasitic and holoparasitic plants, respectively, whose compositions depend on the host. Thus, Cabezas *et al*. (2009) found alkaloids in *T. verticillatus* parasitizing *Berberis montana*, an alkaloid-rich species, but not *Schinus montanus*, a species lacking alkaloids; moreover, the alkaloids in *T. verticillatus* were either the same as those found in *B. montana* or biosynthetically derived from them. The qualitative pattern of alkaloids found in *C. chilensis* was the same as that found in the host, *Sophora macrocarpa* (García *et al*., 1995).

TABLE 1
Studies on the isolation of alkaloids from the native flora of Chile. Currently accepted botanical names are used (http://www2.darwin.edu.ar/Proyectos/FloraArgentina/BuscarEspecies.asp); they may be different from those used in the papers cited. Infraspecific taxa have not been considered independently.

Family	Species	Alkaloid-type	Reference
Amaryllidacee	*Rhodophiala ananuca*	Phenanthridine	Pacheco *et al*., 1978, 1982.
Apocynaceae	*Skytanthus acutus*	Monoterpene alkaloids	Adolphen *et al*., 1967.
Aristolochiaceae	*Aristolochia bridgesii*	Nitrophenanthrene	Urzúa *et al*., 2009
Aristolochiaceae	*Aristolochia chilensis*	Nitrpohenanthrene, aporphine, proaporphine	Urzúa *et al*., 1982, 1983, 1987; Urzúa and Rojas, 1990
Asteraceae	*Chersodoma jodoppapa*	Secopyrrolizidine	Morales *et al*., 1986.
Asteraceae	*Senecio erraticus*	Pyrrolizidine	Reina *et al*., 1993.
Asteraceae	*Senecio glaber*	Pyrrolizidine	Reina *et al*., 1993.
Asteraceae	*Senecio illinitus*	Pyrrolizidine	González *et al*., 1986.
Asteraceae	*Senecio microphyllus*	Pyrrolizidine	Reina *et al*., 1993.
Asteraceae	*Senecio miser*	Pyrrolizidine	Reina *et al*., 2001.
Asteraceae	*Senecio murorum*	Pyrrolizidine	Villarroel *et al*., 1988.
Asteraceae	*Senecio patagonicus*	Pyrrolizidine	Villarroel *et al*., 1985, 1997.
Asteraceae	*Senecio phillipicus*	Pyrrolizidine	González *et al*., 1986.
Asteraceae	*Senecio portalesianus*	Acylpyrrolizidine	Jakupovic *et al*., 1991.
Atherospermataceae	*Laurelia sempervirens*	Bisbenzylisoquinoline, seco-bisbenzylisoquinoline	Bianchi *et al*., 1962; Urzúa *et al*., 1975; Cassels and Urzúa, 1985; Urzúa and Vásquez, 1993; Schmeda-Hirschman et al., 1996.

Atherospermataceae	*Laureliopsis philippiana*	Aporphine, isoquinoline, benzyltetrahydroisoquinoline, bisbenzylisoquinoline	Urzúa and Cassels, 1975, 1978, 1982; Zabel *et al*., 1979; Staerk *et al*., 2009.
Berberidaceae	*Berberis actinacantha*	Pseudobenzylisoquinoline, bisbenzylisoquinoline, isoindolobenzazepine, protoberberine, benzylisoquinoline dimer	Fajardo *et al*., 1979a; Weiss *et al*., 1984; Valencia *et al*., 1984a, 1984b; Urzúa et al., 1985; Fajardo *et al*., 1986.
Berberidaceae	*Berberis chilensis*	Bisbenzylisoquinoline	Torres, 1989; Torres *et al*., 1979a,b.
Berberidaceae	*Berberis darwinii*	Pseudobenzylisoquinoline, isoindolobenzazepine, protoberberine, isoindolobenzazocine, isoindoloisoquinoline	Valencia *et al*., 1984a, 1984b, 1984c, 1985.
Berberidaceae	*Berberis empetrifolia*	Proaporphine-benzylisoquinoline dimer, aporphine-benzylisoquinoline dimer,	Shamma *et al*., 1973; Fajardo *et al*., 1981, 1982a, 1982b, 1982d, 1983; 1985b 1985c, Guinaudeau *et al*., 1982 Hussain *et al*., 1989.
Berberidaceae	*Berberis ilicifolia*	Benzylisoquinoline dimer	Fajardo *et al*., 1996.
Berberidaceae	*Berberis microphylla*	Pavine, benzylisoquinoline, bisbenzylisoquinoline, seco-bisbenzylisoquinoline	Fajardo *et al*., 1979a, 1979b, 1981, 1987; Leet *et al*., 1983, 1984.
Berberidaceae	*Berberis montana*	Protoberberin, benzylisoquinoline, proaporphine, aporphine	Fajardo *et al*., 1986; Fajardo, 1992; Fajardo *et al*., 2009; Cabezas *et al*., 2009.
Berberidaceae	*Berberis valdiviana*	Isoquinoline (cularine), isoindolobenzazepine, protoberberine, proaporphine-benzylisoquinoline dimer, aporphine-benzylisoquinoline dimer, noraporphine-benzylisoquinoline dimer	Shamma *et al*., 1973; Weiss *et al*., 1984; Firdous *et al*., 1984, 1985; Guineadeau *et al*., 1982; Valencia *et al*., 1984b.
Bignoniaceae	*Argylia radiata*	Monoterpene alkaloid	Bianco *et al*., 2002.
Boraginaceae	*Heliotropium floridum*	Pyrrolizidine	Reina *et al*., 1997.
Boraginaceae	*Heliotropium megalanthum*	Pyrrolizidine	Reina *et al*., 1998.
Cactaceae	*Browningia candelaris*	β-Phenethylamine	Echeverría and Niemeyer, 2012.
Cactaceae	*Trichocereus chiloensis*	β-Phenethylamine	Cortés *et al*., 1972.
Campanulaceae	*Lobelia bridgesii*	Pyridyl-pyrrolidine	Marambio *et al*., 1999
Campanulaceae	*Lobelia polyphylla*	Norlobelanidine	Weinges *et al*., 1972
Campanulaceae	*Lobelia tupa*	Pyridyl-pyrrolidine	Marambio *et al*., 1999
Celastraceae	*Maytenus disticha*	Nicotinoyl sesquiterpene	Alarcón *et al*., 1998.
Celastraceae	*Maytenus magellanica*	Nicotinoyl sesquiterpene	Kennedy *et al*., 2001.
Cuscutaceae	*Cuscuta chilense*	Quinolizidine	García *et al*., 1995.
Elaeocarpaceae	*Aristotelia chilensis*	Indolenine, quinoline	Torres and Comin, 1975; Gopalakrishna *et al*., 1978; Bhakuni *et al*., 1976; Bittner *et al*., 1978 ; Zabel *et al*., 1980; Watson *et al*., 1989; Céspedes *et al*., 1990, 1993; Silva and Bittner, 1992; Silva *et al.* 1997; He *et al*., 1997.
Ephedraceae	*Ephedra gracilis*	Ephedra	Hegnauer, 1962.
Euphorbiaceae	*Croton chilensis*	Morphine, aporphine	Bittner *et al*., 2001.
Fabaceae	*Lupinus microcarpus*	Quinolizidine	Wink *et al*., 1995.
Fabaceae	*Prosopis alba*	β-phenethylamine, piperidine	Astudillo *et al*., 1999.
Fabaceae	*Prosopis chilensis*	β-phenethylamine, tryptamine	Astudillo *et al*., 2000.
Fabaceae	*Prosopis tamarugo*	β-phenethylamine, pyrrolizine, tryptamine	Astudillo *et al*., 2000; Schmeda-Hirschmann and Jakupovic, 2000.
Fabaceae	*Sophora fernandeziana*	Quinolizidine, piperidine	Hoeneisen *et al*., 1993.
Fabaceae	*Sophora macrocarpa*	Quinolizidine	Negrete *et al*., 1982, 1983; Hoeneisen *et al*., 1993.
Fabaceae	*Sophora masafuera*	Quinolizidine, piperidine	Hoeneisen *et al*., 1993.
Fabaceae	*Sophora microphylla*	Quinolizidine, piperidine	Urzúa and Cassels, 1970; Hoeneisen *et al*.1993.

Fabaceae	*Sophora tetraptera*	Quinolizidine	Urzúa *et al*., 1970. Reyes *et al*., 1988.
Lauraceae	*Cryptocarya alba*	Benzyltetrahydroisoquinoline	Urzúa *et al*., 1975.
Loranthaceae	*Tristerix verticillatus*	Isoquinoline	Cabezas *et al*., 2009.
Lycopodiaceae	*Lycopodium confertum*	Paniculine	Garland and Muñoz *et al*., 1982; Muñoz *et al*., 1990.
Lycopodiaceae	*Lycopodium magellanicum*	Paniculine	Castillo *et al*., 1976a; Loyola *et al*., 1979.
Lycopodiaceae	*Lycopodium paniculatum*	Paniculine	Castillo *et al*., 1975, 1976b; Morales *et al*. 1979.
Monimiaceae	*Peumus boldus*	Aporphine, benzylisoquinoline	Hughes *et al*., 1968a,b; Genest *et al*., 1969; Urzua and Acuña, 1983, Urzúa and Torres, 1984, Asencio *et al*., 1993.
Rhamnaceae	*Colletia hystrix*	Benzylisoquinoline	Sánchez and Torres *et al*., 1971.
Rhamnaceae	*Colletia spinosissima*	Quaternary aphorphine	Sánchez and Comin, 1967
Rhamnaceae	*Discaria chacaye*	Aporphine, benzylisoquinoline, cyclopeptide	Pacheco *et al*., 1973; Silva *et al*., 1974; Rivera *et al*., 1984; Torres *et al*.,1984; Correa *et al*., 1987.
Rhamnaceae	*Retanilla ephedra*	Cyclopeptide	Bhakuni *et al*. 1974.
Rhamnaceae	*Trevoa quinquenervia*	Benzylisoquinoline, benzyltetrahydroisoquinoline	Torres and Piña, 1989; Alarcón *et al*., 2011.
Rutaceae	*Fagara mayu*	β-Carboline, Benzyltetrahydroisoquinoline, furoquinoline, benzophenanthridine, ephedra	Benages *et al*. 1974; Torres and Cassels, 1978. Assem *et al*., 1979, 1983;
Rutaceae	*Pitavia punctata*	Furoquinoline	Silva *et al*. 1971.
Solanaceae	*Cestrum parqui*	Steroidal	Silva *et al*., 1962.
Solanaceae	*Dunalia spinosa*	Amine-whitanolide, pyridyl-pyrrolidine	Espinoza *et al*., 2012.
Solanaceae	*Fabiana imbricata*	Tetrahydroquinoline	Edward and Elmore, 1962.
Solanaceae	*Latua pubiflora*	Tropane	Silva and Mancinelli, 1959; Muñoz and Casale, 2003.
Solanaceae	*Nicotiana acuminata*	Pyridyl-pyrrolidine	Saitoh *et al*., 1985.
Solanaceae	*Nicotiana corymbosa*	Pyridyl-pyrrolidine	Saitoh *et al*., 1985.
Solanaceae	*Nicotiana longibracteata*	Pyridyl-pyrrolidine	Saitoh *et al*., 1985.
Solanaceae	*Nicotiana miersii*	Pyridyl-pyrrolidine	Saitoh *et al*., 1985.
Solanaceae	*Nicotiana pauciflora*	Pyridyl-pyrrolidine	Saitoh *et al*., 1985.
Solanaceae	*Nicotiana petunoides*	Pyridyl-pyrrolidine	Saitoh *et al*., 1985.
Solanaceae	*Nicotiana solanifolia*	Pyridyl-pyrrolidine	Saitoh *et al*., 1985.
Solanaceae	*Nicotiana undulata*	Pyridyl-pyrrolidine	Saitoh *et al*., 1985.
Solanaceae	*Schizanthus grahamii*	Tropane	San Martín *et al*., 1987; Hartmann *et al*., 1990; Muñoz *et al*., 1991; Humam *et al*., 2005; Bieri *et al*., 2006; Cretton *et al*., 2011.
Solanaceae	*Schizanthus hookerii*	Tropane	Gambaro *et al*., 1983; San Martín *et al*. 1980.
Solanaceae	*Schizanthus integrifolius*	Tropane	Muñoz *et al*., 1994.
Solanaceae	*Schizanthus litoralis*	Tropane	Muñoz *et al*., 1996.
Solanaceae	*Schizanthus tricolor*	Tropane	Humam *et al*., 2006, 2007, 2011; Cretton *et al*., 2010.
Solanaceae	*Solanum chilense*	Glycosteroid	Schreiber, 1979.
Solanaceae	*Solanum crispum*	Steroidal	Bianchi *et al*., 1965; Sato *et al*., 1969; Schreiber, 1979; Reyes *et al*., 1988.
Solanaceae	*Solanum furcatum*	Glycosteroid	Briggs *et al*., 1961.
Solanaceae	*Solanum ligustrinum*	Glycosteroid	Delporte *et al*., 1998.
Solanaceae	*Solanum lycopersicoides*	Glycosteroid	Oleszek *et al*., 1986.
Solanaceae	*Solanum marginatum*	Steroidal	Schreiber, 1979.
Solanaceae	*Schizanthus pinnatus*	Tropane, glycosteroid	Urzúa and Cassels, 1972; Ripperger, 1979; De la Fuente *et al*., 1988.
Solanaceae	*Schizanthus porrigens*	Tropane	Muñoz and Cortés, 1998.

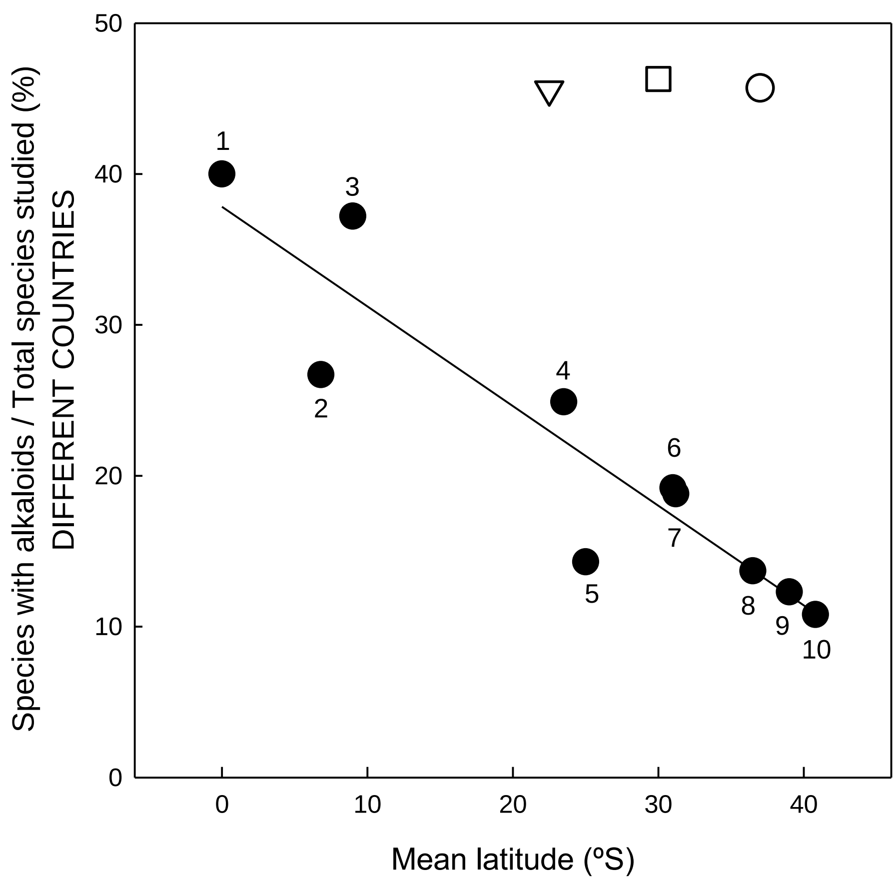
Solanaceae	*Solanum valdiviense*	Steroidal	Reyes *et al*., 1988.
Solanaceae	*Vestia foetida*	β-Carboline	Faini *et al*., 1978, 1980.

The occurrence of alkaloids in the Chilean native flora was analyzed using two different metrics: i) the proportion of alkaloid-containing species in relation to the total number of species analyzed, and ii) the proportion of alkaloid-containing species in relation to the total number of species in the flora examined.

A screening of the Chilean native flora for alkaloids showed that 45.7% of the species analyzed contained them (Bustamante *et al*., 2006). Similar studies have been performed with the floras of other countries and a significant and negative linear correlation has been found between the percentage of alkaloid bearing species in relation to species analyzed and mean latitude of the country (Levin 1976). Figure 1 shows such data and includes the point for Chile; this point clearly deviates from the line, as do the points for India and Pakistan. These three countries share a particularly wide range of ecosystems, mainly on account of extreme altitudinal and latitudinal gradients.

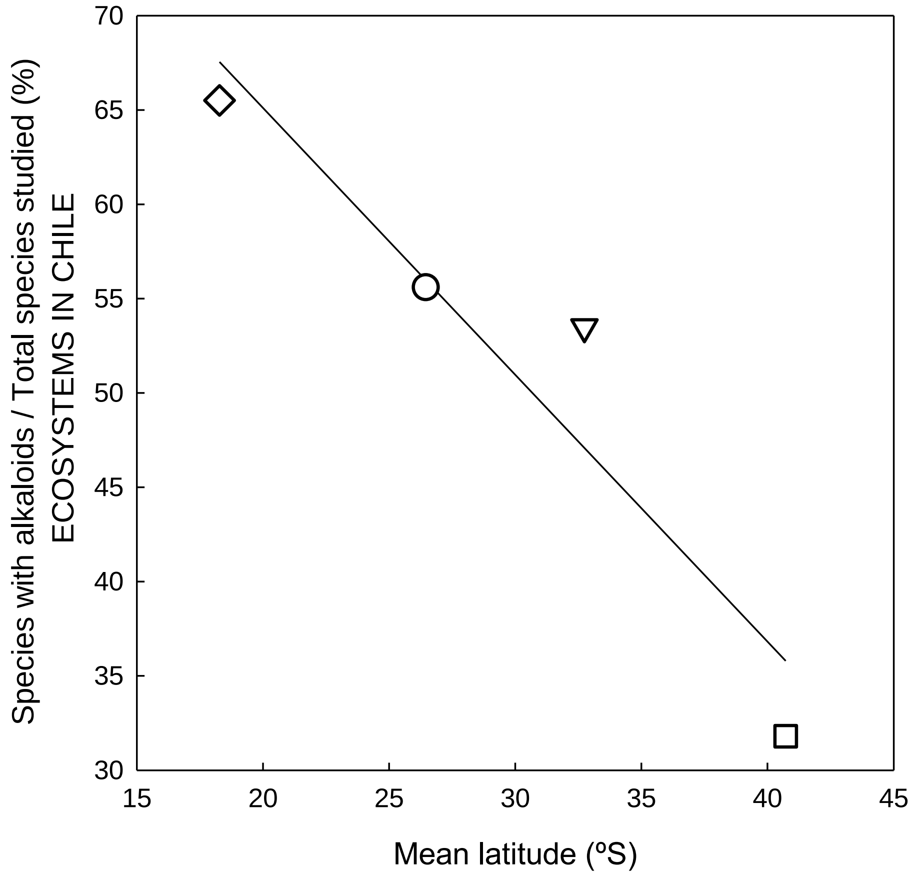
FIGURE 1

Latitudinal effect on alkaloid richness of the flora of different countries: 1 = Kenya, 2 = New Guinea, 3 = Ethiopia, 4 = Mexico, 5 = Australia, 6 = Uruguay, 7 = Israel, 8 = United States, 9 = Turkey, 10 = New Zealand, triangle = India, square = Pakistan, circle = Chile. Data from Levin (1976) and this work.



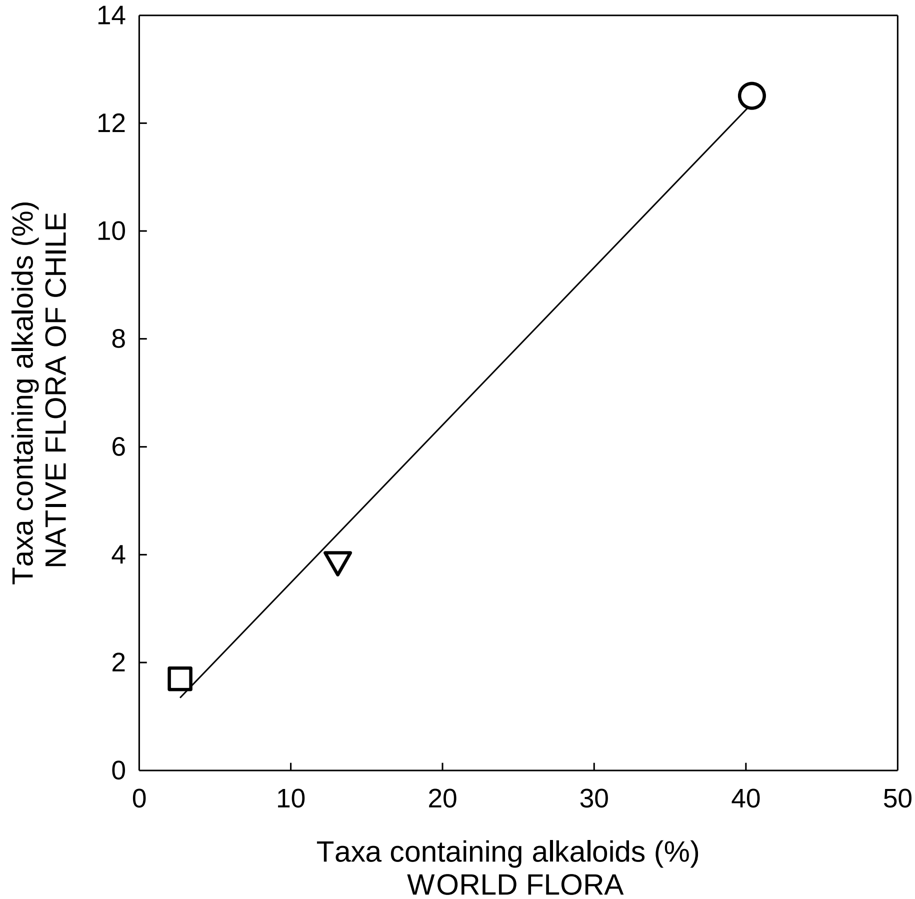
A further analysis of the latitudinal effect on alkaloid richness of the flora of Chile was performed by considering different ecosystems which occur at different mean latitudes. The results, presented in figure 2, show a negative linear relationship between the proportion of alkaloid-containing species in relation to the total number of species analyzed, and the mean latitude of the respective ecosystem. These two analyses show the consistency of the data on the Chilean flora with data from the world flora.

FIGURE 2
Effect of latitude on alkaloid richness of different ecosystems in Chile: rhomboid = Andean tropical, circle = desert, inverted triangle = mediterranean, square = oceanic



The number of alkaloid-containing taxa, as judged by published reports, represents a low proportion of the Chilean flora; thus, alkaloids have been reported in only 12.5% of the families, 3.9% of the genera and 1.7% of the native species occurring in Chile. When these figures are compared with corresponding values at the world scale, *i.e.*., 40.4% of the families, 13.1% of the genera and 2.7% of the species (Cordell *et al*., 2001; Stevens, 2008), a proportionality between the two sets of data is revealed, the slope of the correlation being 0.29. This suggests that the alkaloid potential of the Chilean native flora has been exploited to the extent of only 29%.

FIGURE 3
Comparison of flora of the world and native flora of Chile in terms of percentage of alkaloid-containing taxa at family (circle), genera (triangle) and species (square) levels

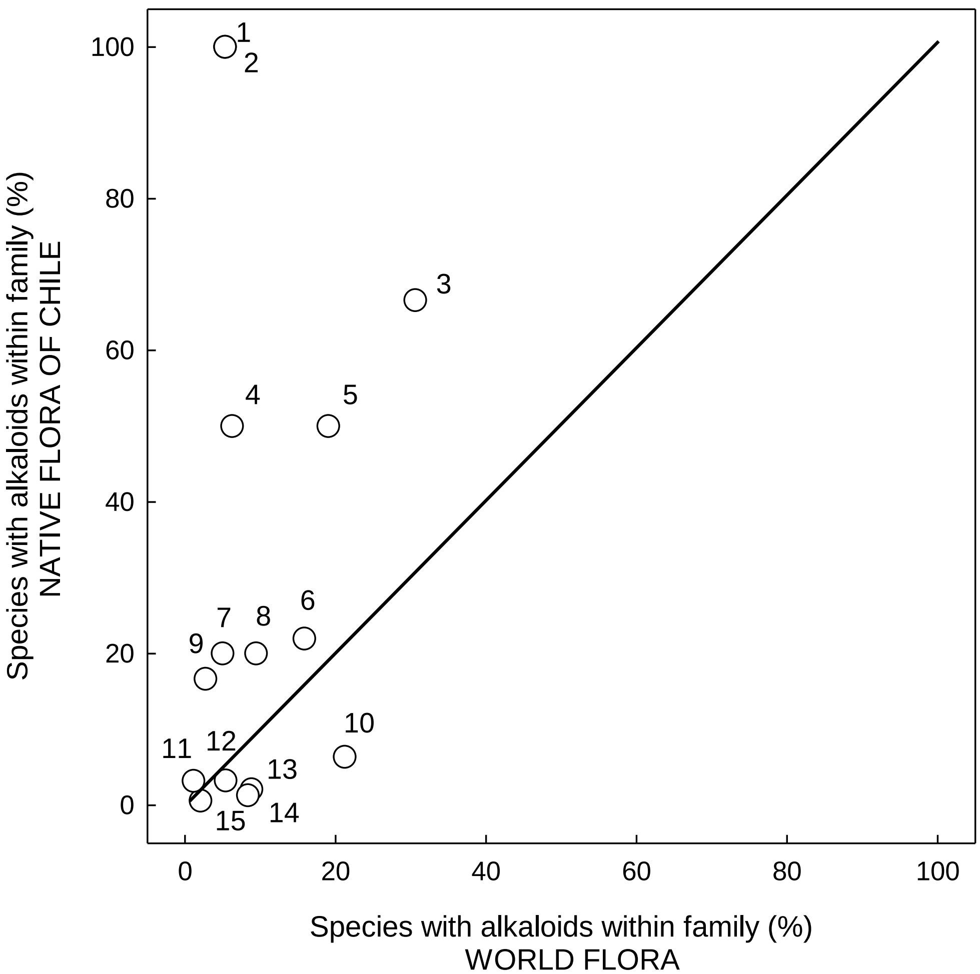


Cordell *et al*. (2001) have made a thorough analysis of the occurrence of alkaloids in the world flora, on the basis of NAPRALERT, the largest database on natural products chemistry and pharmacology (http://www.napralert.org/). Their results can be used as a standard for comparison for the distribution of alkaloids in the Chilean flora. Such comparison is presented in figure 4, which shows the percentage of alkaloid-containing species within families in both floras. The line drawn in the figure, with a slope equal to 1, represents the hypothetical situation if alkaloids were equally frequent in families of the floras of Chile and the world.

In families situated above the line in figure 4, a higher proportion of alkaloid-containing species occurs in the Chilean flora than in the world flora, *i.e*. in such families the Chilean flora appears richer in alkaloids than the flora of the world. However, such conclusion should be treated with caution because most of those families contain very few species (families numbered 1-6, 8 and 9 in figure 4 have between 2 and 8 species, whereas families numbered 7 and 10-15 in figure 4 have between 34 and 837 species), thus making their apparent richness in alkaloids more a matter of chance. This point may be illustrated with the former family Monimiaceae. While worldwide 24 out of 450 (5.3%) species have been shown to contain alkaloids (Cordell *et al*., 2001), in Chile all three species (now assigned to the Monimiaceae and Atherospermataceae), *i.e*. 100% of the species, contained alkaloids. While the former proportion can be thought of as a fair representation of alkaloid richness in the family, the second is a more discrete and hence volatile figure. Another clear example is the Rutaceae: 459 out of 1500 species contain alkaloids wordwide (30.6%), whereas 2 of 3 species in Chile (66.7%) contain them.

FIGURE 4

Percentage of alkaloid-containing species in families of the flora of Chile and the world [in parenthesis, the number of species of the flora of Chile (Marticorena and Quezada, 1985) and of the flora of the world (Cordell *et al*., 2001). Families are: 1,2 = Monimiaceae (1,450 including Atherospermataceae) and Atherospermataceae (2); 3 = Rutaceae (3,1500); 4 = Celastraceae (4,800); 5 = Apocynaceae (2,2100); 6 = Rhamnaceae (20,900); 7 = Solanaceae (134,2800); 8 = Lauraceae (5,2000); 9 = Loranthaceae (8,700); 10 = Berberidaceae (50,650); 11 = Euphorbiaceae (34,7500); 12 = Fabaceae (293,16400); 13 = Boraginaceae (97,2000); 14 = Cactaceae (174,1650) 15 = Asteraceae (837,21000)



On the other hand, in families situated below the line of figure 4 a lower proportion of alkaloid-containing species is found in the Chilean flora than in the world flora, *i.e.* in these families the Chilean flora appears as poorer in alkaloids than the flora of the world. The families below the line (families numbered 11-15 in figure 4) are all more biodiverse than families above the line (with the exception of family numbered 7, the Solanaceae, discussed below). Hence, the frequency of occurrence of alkaloids can be more accurately compared with the situation worlwide. The Solanaceae appears above the line on account of the poor generical representation in the Chilean flora reported, *i.e.* 22 of the 27 alkaloid-containing species belong to only three genera, *Nicotiana*, *Schizanthus* and *Solanum*. The data suggests that families falling below the line should be studied further because they should include numerous species with alkaloids.

The reports on the Chilean flora suggest that the analytical efforts have not been distributed homogenoeusly. Thus, reports on alkaloid-containing taxa from Chile are concentrated in a few families and genera, *i.e*. out of the 87 species where alkaloids have been found, 27, 9, and 8 were found in the families Solanaceae, Asteraceae, and Fabaceae, respectively (the rest being distributed among 20 families), and 8, 8, 7 and 7 in the genera *Berberis, Nicotiana, Solanum* and *Schizanthus*, respectively (the rest being distributed among 35 genera).

The report on the distribution of alkaloids in the world flora showed that several families, present also in Chile, are particularly rich in alkaloids, *e.g.* Convolvulaceae, Ephedraceae, Lamiaceae, Liliaceae, Papaveraceae, Phytolaccaceae, Ranunculaceae and Zygophyllaceae (Cordell *et al*., 2001). If the percentage of occurrence of alkaloids in those families in the world flora is multiplied by the number of species in each family in Chile, it is predicted that at least 18 species from these families should contain alkaloids.

Most work on alkaloids in Chilean species has been published by Chilean researchers with occasional collaboration of foreign colleagues, and most reports have been published more than 10 years ago; in other words, the interest in isolating new alkaloids from native Chilean plants seems to be vanishing. Given the importance of alkaloids in the cure of widespread diseases, the isolation, structural characterization and biological activity of alkaloids from the native flora of Chile should be pursued.

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