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Phytochemistry 66 (2005) 469–480
PHYTOCHEMISTRY
www.elsevier.com/locate/phytochem

Calystegines as chemotaxonomic markers in the Convolvulaceae ☆

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Received 8 September 2004; received in revised form 20 December 2004
Available online 26 January 2005

Abstract

An extended GC–MS study of 129 convolvulaceous species belonging to 29 genera (all 12 tribes) including the results of a previous survey (65 spp.) revealed the occurrence of one to six polyhydroxy alkaloids of the nortropane type (calystegines) in 62 species belonging to 22 genera of all tribes except the unique parasitic Cuscuteae. The large genus *Ipomoea* turned out to comprise calystegine-positive species in at least eight out of ten sections checked. The number of the calystegines used as reference compounds has been increased from seven (previous survey) to 11 (present study). Furthermore, the results concerning these additional four alkaloids could also be completed for all species of the previous survey. The plant material (epigeal vegetative parts and/or roots, flowers, fruits/seeds) was obtained from collections in the wild from a wide range of tropical, subtropical, and temperate locations of all continents as well as from cultivation in the greenhouse. All plant organs turned out to be potential locations for the occurrence of these metabolites though they are detectable often only in certain organs of a given species. Three genera (*Cuscuta*, *Operculina*, *Polymeria*) might have lost the ability to synthesize these plesiomorphic characters in the course of the evolution since the examination of several different organs and/or provenances of five species each failed to show calystegines as constituents. Nevertheless, the present data clearly demonstrate that the occurrence of calystegines is an almost consistent trait in the Convolvulaceae in principle, from basal to most advanced tribes.

Keywords: Convolvulaceae; GC–MS analysis; Tropane alkaloids; Polyhydroxy alkaloids; Calystegines; Castanospermine; Swainsonine; Glycosidase inhibitors; Chemotaxonomy

1. Introduction

Polyhydroxy alkaloids, e.g., the calystegines (nortropanes) bind specifically to the active sites of glycosidases inhibiting the enzymes. Thus, they have aroused increasing interest as, e.g., potential antiviral, anticancer, and antidiabetic agents. From the ecological point of view such compounds may cause intoxications in cattle (Asano et al., 2000 and literature therein) and are also toxic for vertebrates, insects, and microbes (Fellows et al., 1989 and literature therein). Furthermore, they exhibit antifeedant effects against lepidopterans (Simmonds et al., 1990). However, it is not yet clear if there is a physiological role

☆ Part 17 in the series "Phytochemistry and Chemotaxonomy of the Convolvulaceae". For part 16, see Jenett-Siems et al. [Phytochemistry, 66 (2005) 223–231].

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0031-9422/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.phytochem.2004.12.024

of polyhydroxy alkaloids in general and of calystegines in particular for the producing plant species itself (Dräger, 2004; Hoeke and Dräger, 2004).

The calystegines seem to be confined to the two major Solanales families, Convolvulaceae and Solanaceae, as well as to the unrelated Moraceae. To date the structures of 15 calystegines have been elucidated including five trihydroxynortropanes (A_3, A_5–A_8), six tetrahydroxy congeners (B_1–B_6), and two pentahydroxy derivatives (C_1, C_2) (see Fig. 1). Besides free calystegines, several glycosides could be isolated from solanaceous species. In addition, the N-methylated congeners of the calystegines B_2 and C_1, respectively, have been found again in solanaceous species (Asano et al., 2000; Dräger, 2004). The occurrence of calystegines in the family Solanaceae is documented in the literature for 15 genera (out of 92) covering 32 species (out of 2300) (Table 3). In the sister family Convolvulaceae these alkaloids were found in *Calystegia sepium* and *Convolvulus arvensis* (Tepfer et al., 1988), two further *Calystegia* spp. (Molyneux et al., 1995) and seven *Ipomoea* taxa (Asano et al., 2001). In our previous study on the occurrence and distribution of these compounds in the Convolvulaceae comprising 65 species (out of 1850) from 22 genera (out of 55) after all 30 species belonging to 15 genera were found to be calystegine-positive (Schimming et al., 1998).

Our present study has been extended considerably in several respects: (1) It comprises another 64 species including for the first time also Australian taxa with the consequence that all continents are represented now. (2) Again for the first time the rare genera *Cardiochlamys*, *Humbertia*, *Rapona* (all endemic to Madagascar), and *Hildebrandtia* (East Africa/Madagascar/Arabia) altogether classified as basal (Stefanović et al., 2003), as well as the more advanced genera *Polymeria* (endemic to Australia) and *Astripomoea* (endemic to Africa) are involved. (3) We have been able to include species from not yet investigated sections of the large genera *Ipomoea* and *Merremia*, respectively. (4) The number of species in certain genera which had turned out already in the previous study to be calystegine-positive has been increased disproportionately (the largest genus *Ipomoea* by additional 21 species, comprising now in total 38 species; the large genus *Convolvulus* by 13 (now in total: 18), the basal genus *Erycibe* by 3 (now in total: 5) in order to confirm these previous findings. (5) In our first study two genera (*Jacquemontia*, *Operculina*) did not show any occurrence of calystegines in different samples of several species. By including further species and/or organs of these genera we wanted to find out if these will support this previous finding or not. (6) Our former study was based only on seven calystegines whereas now we could integrate four additional congeners. This also means that we are able to enhance the results of the former 65 species by these additional polyhydroxylated alkaloids. Thus, we want to report on the occurrence/the lack of all these metabolites in 129 species belonging to 29 genera which include

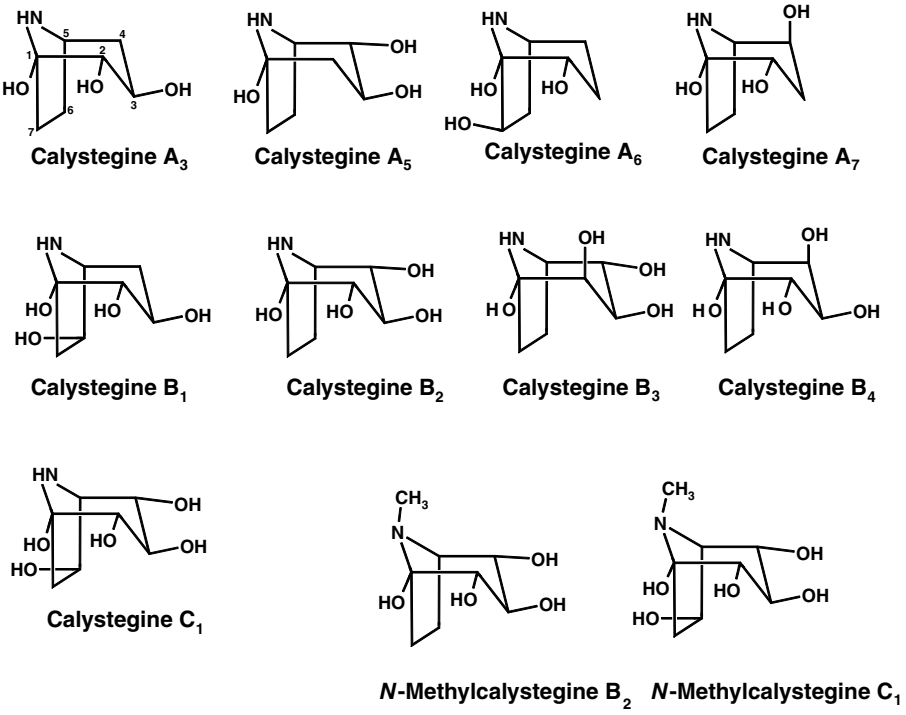

Fig. 1. Structure of the calystegines and *N*-methylcalystegines included in this study.