

THE OCCURRENCE OF IRIDOID GLYCOSIDES IN THE LABIATAE

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SUMMARY

Iridoid glycosides were found in many species of the following taxa of the *Labiatae*: *Prostantheroideae*, *Ajugoideae*, *Prasioideae*, *Scutellarioideae*, *Stachydoideae-Marrubieae* and *St.-Stachydeae*. Iridoid glycosides were not found in any species of the following subfamilies: *Rosmarinoideae*, *Ocimoideae*, *Lavanduloideae*, and *Stachydoideae* (except the two tribes mentioned). The former group of taxa coincides with the taxa having binucleate, tricolpate pollen grains, while the latter group has trinucleate, hexacolpate pollen grains, the binucleate, tricolpate *Pogostemoneae* being exceptional.

Of the many iridoid glycosides present in the binucleate, tricolpate part of the *Labiatae*, a considerable proportion is still unidentified and the chemical structures of several of them are as yet unknown. Some of the latter were isolated and characterized by their specific optical rotations and R_f -values on paper chromatograms.

1. INTRODUCTION

Since the occurrence of iridoid glycosides in some *Labiatae* was indicated by colour reactions (TRIM & HILL 1952), a number of publications have appeared on iridoid glycosides in certain members of this family; the structures of several of these glycosides have been elucidated. Harpagide (I), monomelittoside (II) and derivatives have been found in *Melittis melissophyllum* (SCARPATI *et al.* 1965, 1967a, b), harpagide and acetylharpagide in *Betonica foliosa* (LITVINENKO *et al.* 1968). Chromatographic evidence for the presence of these glycosides in *Ajuga reptans*, several *Galeopsis* and *Stachys* species, and in *Teucrium montanum* was obtained by WIEFFERING (1966). In addition the occurrence of harpagide-type iridoids in *Lamium galeobdolon* (ADEMA 1968), and in a number of *Teucrium* species (FIKENSCHER & HEGNAUER 1969) has been reported. The iridoid glycosides lamiol (III), lamiide (IV) and some related compounds which are present in *Lamium amplexicaule* have been isolated and studied (SCARPATI *et al.* 1967c, 1969), whereas chromatographic evidence for the presence of *Lamium*-type glycosides in *Stachys hirta* was reported (ADEMA 1968). Apart from harpagide WIEFFERING (1966) found two other presumably iridoid substances in *Galeopsis tetrahit* by means of paper chromatography, the structure of one of which (galiridoside, V) was elucidated by STICHER (1970a, b). From *Physostegia virginiana* bisdesoxydihydromonotropeoside (VI) was isolated and characterized by RIMPLER *et al.* (1970).

In the present study the occurrence of iridoid glycosides in the *Labiatae* was investigated and the results were compared with the subdivisions of the family reported in the literature.

2. MATERIALS AND METHODS

Vegetative parts used for extraction were taken from specimens cultivated in the Botanical Garden of this laboratory; in some cases samples were collected from the natural habitats. Most of the fruit samples tested were obtained *via* the seed-lists of horti. To avoid erroneous results caused by misnamed samples either extracts were prepared in duplicate or triplicate from samples of two or three horti; or from the samples used for extraction a part was sown and the resulting plants were identified.

The preparation of extracts, the isolation of glycosides and the technique of paper chromatography were performed as described previously (KOOIMAN 1970).

3. RESULTS

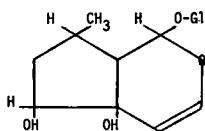
The investigated species of the subfamilies *Prostantheroideae*, *Ajugoideae*, *Prasioideae*, *Stachyoideae* (tribes *Pogostemoneae*, *Marrubieae*, and *Stachydeae*), and *Scutellarioideae* are recorded in *table 1*. They are arranged according to the system in Engler's Syllabus (MELCHIOR 1964). The results of the paper chromatographic examination are given in the last column of the table.

In the *Prostantheroideae* catalpol occurs presumably in *Hemiandra*, while as yet unknown, probably iridoid glycosides occur in other species of this subfamily.

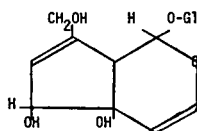
The *Ajugoideae* are rich in species containing iridoid glycosides. Although in several *Teucrium* species no glycosides were encountered, several other species of this genus contain glycosides which resemble glycosides of the harpagide type by their paper chromatographic behaviour. Similar glycosides were found in *Ajuga* species, although the colours of the spots on the chromatograms were distinct from those of the *Teucrium* glycosides. From *Ajuga reptans* a glycoside having R_F 0.81 in the n.butanol-ethanol-water (40:11:19 v/v) solvent system and $[\alpha]_D^{64}$ was isolated (*Ajuga* glycoside A); in addition a glycoside with R_F 0.54 and $[\alpha]_D^{97}$ (*Ajuga* glycoside B) and one with R_F 0.36 and $[\alpha]_D^{81}$ (all in water) (*Ajuga* glycoside C) were isolated. From *Teucrium arduinii* the following glycosides were isolated: *Teucrium* glycoside A (R_F 0.81), B (R_F 0.55), and C (R_F 0.36, $[\alpha]_D^{66}$ (water)). Although the chromatographic mobilities of the glycosides C are similar to the mobility of harpagide, the $[\alpha]_D$ -values are different, harpagide having $[\alpha]_D^{158.6}$ (ethanol).

Of the *Prasioideae*, *Prasium majus* contains at least two iridoid glycosides, one of which occurs as a major component; it has R_F 0.17 and $[\alpha]_D^{25}$ (water) and behaves on the paper chromatogram as melittoside ($[\alpha]_D^{29}$).

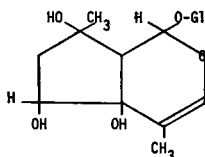
None of the *Pogostemoneae* tested appeared to contain iridoid glycosides, whereas in the *Marrubieae* most *Sideritis* species contain harpagide-type glycosides. One of the glycosides of *Sideritis syriaca* has R_F 0.17 and $[\alpha]_D^{29}$ (water) and is probably identical with melittoside. The other major glycoside has R_F 0.36 and $[\alpha]_D^{162}$ (water) and -145 (ethanol) and is probably identical with harpagide. In many *Stachydeae* harpagide- and monomelittoside-type glycosides occur; apparently many other *Stachydeae* lack iridoid glycosides. In



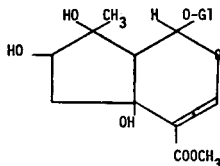
I harpagide



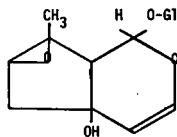
II monomelittoside



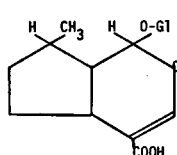
III lamiol



IV lamiide



V galiridoside



VI bisdesoxydihydromonotropeoside

some *Lamium* species lamiol- and (or) lamiide-type glycosides were found.

In the vegetative parts of several *Phlomis* species *Phlomis* glycoside B (R_F 0.34) occurs, whereas in the fruits both *Phlomis* glycosides A and B occur. *Phlomis* glycoside A (R_F 0.90) is an ester of *Phlomis* glycoside B since treatment of compound A with alkali resulted in compound B (paper chromatographic evidence).

From vegetative material of *Physostegia virginiana* three presumably iridoid compounds were isolated, one component having R_F 0.64 and $[\alpha]_D -65^\circ$, the second R_F 0.53 and $[\alpha]_D -75^\circ$, and the third R_F 0.38 and $[\alpha]_D -104^\circ$ (all in water). It is not probable that any of these glycosides is identical with bisdesoxydihydromonotropeoside isolated from this species by RIMPLER *et al.* (1970) and which has $[\alpha]_D -90^\circ$ (ethanol); none of the three glycosides behaves as an acid which the latter compound should do.

Leaves of *Leonurus cardiaca* contain at least three glycosides. *Leonurus* glycoside A has R_F 0.63–0.64 and $[\alpha]_D -98^\circ$, glycoside B R_F 0.51–0.52 and $[\alpha]_D -76^\circ$, whereas glycoside C has R_F 0.43–0.44 and $[\alpha]_D -97^\circ$ (all in water).

Catalpol was isolated from *Scutellaria altissima* and identified by its melting point and specific optical rotation. Judging from the results of paper chromatographic analysis and of the characteristic colour reaction of catalpol its presence in several other *Scutellaria* species is hardly to be doubted.

Of the subfamilies and tribes not recorded in *table 1* species (numbers tested in parentheses) of the following genera have been tested, all of which appeared to lack iridoid glycosides.

<i>Rosmarinoideae:</i>	<i>Rosmarinus</i> (1)
<i>Ocimoideae:</i>	<i>Aeolanthus</i> (1), <i>Alvesia</i> (1), <i>Coleus</i> (2), <i>Hyptis</i> (1), <i>Moschosma</i> (1), <i>Ocimum</i> (2), <i>Platostoma</i> (1), <i>Plectranthus</i> (2), <i>Pycnostachys</i> (1), <i>Solenostemon</i> (1).
<i>Lavanduloideae:</i>	<i>Lavandula</i> (2)
<i>Stachydoideae-Saturejeae:</i>	<i>Acinos</i> (1), <i>Bystropogon</i> (1), <i>Calamintha</i> (1), <i>Coridothamnus</i> (1), <i>Hedeoma</i> (1), <i>Hyssopus</i> (1), <i>Lycopus</i> (2), <i>Melissa</i> (1), <i>Mentha</i> (1), <i>Micromeria</i> (2), <i>Monardella</i> (1), <i>Mosla</i> (1), <i>Origanum</i> (1), <i>Perilla</i> (2), <i>Preslia</i> (1), <i>Pycnanthemum</i> (2), <i>Satureja</i> (3), <i>Thymus</i> (3), <i>Ziziphora</i> (2).
— <i>-Lepechinieae:</i>	<i>Lepechinia</i> (3)
— <i>-Hormineae:</i>	<i>Horminum</i> (1)
— <i>-Nepeteae:</i>	<i>Agastache</i> (1), <i>Brittonastrum</i> (1), <i>Cedronella</i> (1), <i>Dracocephalum</i> (3), <i>Glechoma</i> (1), <i>Hymenocrater</i> (1), <i>Lophanthus</i> (1), <i>Moldavica</i> (1), <i>Nepeta</i> (4)
— <i>-Meriandreae:</i>	<i>Meriandra</i> (1), <i>Perovskia</i> (2)
— <i>-Monardeae:</i>	<i>Blephilia</i> (2), <i>Monarda</i> (1)
— <i>-Salviae:</i>	<i>Salvia</i> (4), <i>Schraderia</i> (1)

4. DISCUSSION

Of the family Labiatae 194 species belonging to 80 genera have been tested for the presence of iridoid glycosides in their vegetative and/or generative parts. This means that the material studied covers 40% of the genera and 6.5% of the species of the family. Although the part of the family studied is relatively small, the results are sufficiently consistent to allow the following considerations and conclusions.

It is obvious that the Labiatae contain many species in which iridoid glycosides occur, a rich variety of those glycosides occurring in the family. Of many of them the chemical structures are still unknown. In the present study the method used in examining the presence of iridoid glycosides does not allow to make decisive conclusions on the identity of most of the glycosides met with; in particular, harpagide and monomelittoside were not clearly differentiated from each other, and also their derivatives could not be identified with much probability. A closer study on the identity of many of the glycosides indicated in *table 1* would be highly rewarding.

Whereas so far harpagide and derivatives have been found outside the Labiatae exclusively in *Harpagophytum* (Pedaliaceae) (TUNMANN *et al.* 1962, and other papers; LICHTI *et al.* 1964) and in *Scrophularia* (Scrophulariaceae) (KITAGAWA *et al.* 1967), none of the other known and unknown iridoid glycosides of the La-

Table 1. Iridoid glycosides in the *Labiatae*.

	Organ	Spots
PROSTANTHEROIDEAE		
<i>Hemiandra pungens</i> R. Br.	f	cat
<i>H. pungens</i>	l	cat + cat ester
<i>Microcorys exserta</i> Benth.	f	2 spots
<i>Prostanthera nivea</i> A. Cunn.	l, f	1 spot
<i>P. ovalifolia</i> R. Br.	f	2 spots
AJUGOIDEAE		
<i>Ajuga chamaepitys</i> Schreb.	l, f	ac harp + 2 o
<i>A. genevensis</i> L.	l	harp + ac harp
<i>A. reptans</i> L.	l	harp + 4 o
<i>Teucrium arduinii</i> L.	l	4 spots
<i>T. botrys</i> L.	l	some spots (weak)
<i>T. chamaedrys</i> L.	l, f	some spots
<i>T. cubense</i> Jacq.	l	ac harp + 1 o
<i>T. flavum</i> L.	l	harp + ac harp + 1 o
<i>T. fruticans</i> L.	l	1 spot
<i>T. heterophyllum</i> L'Hérit.	f	—
<i>T. hircanicum</i> L.	l	harp + ac harp
<i>T. marum</i> L.	l	—
<i>T. montanum</i> L.	l	—
<i>T. polium</i> L.	l	2 spots
<i>T. scorodonia</i> L.	l	2 spots
<i>T. vesicarium</i> Mill.	f	—
<i>Tinnea eriocalyx</i> Welw.	f	—
<i>Trichostema parishii</i> Vasey	f	harp + ac harp
PRASIOIDEAE		
<i>Prasium majus</i> L.	l, f	mel + 1 o
STACHYDOIDEAE-POGOSTEMONEAE		
<i>Elsholtzia ciliata</i> (Thunb.) Hylander	l, f	—
<i>Pogostemon cablin</i> (Blanco) Benth.	l, f	—
<i>P. plectranthoides</i> Desf.	l, f	—
STACHYDOIDEAE-MARRUBIEAE		
<i>Leucophaë macrostachys</i> Webb. et Berth.	l, f	—
<i>Marrubium candidissimum</i> L.	l, f	—
<i>M. leonuroides</i> Desr.	l	—
<i>M. peregrinum</i> L.	f	—
<i>M. persicum</i> C.A. Mey	f	—
<i>M. vulgare</i> L.	f	—
<i>Sideritis argosphacelus</i> Clos	l	ac harp + mel
<i>S. canariensis</i> L.	l, f	harp + 1 o
<i>S. euboea</i> Heldr.	l	harp + mel + 2 o
<i>S. glacialis</i> Boiss.	l, f	harp + mel
<i>S. gracilis</i> Barb.	f	—
<i>S. hyssopifolia</i> L.	f	harp + mel
<i>S. libanotica</i> Labill.	l	harp + mel
<i>S. montana</i> L.	l	mel
<i>S. scordioides</i> L.	l	mel + 2 o
<i>S. syriaca</i> L.	l	harp + mel + 2 o
STACHYDOIDEAE-STACHYDEAE		
<i>Anisomeles salviifolia</i> R.Br.	l, f	some spots
<i>Ballota acuta</i> (Moench) Briq.	f	—

	Organ	Spots
<i>B. nigra</i> L.	l, f	—
<i>B. rupestris</i> Vis.	f	—
<i>Cleonia lusitanica</i> L.	f	—
<i>Eremostachys hissanica</i> Regel	f	—
<i>E. labiosiformis</i> (M. Pop.) Knorr.	f	harp
<i>Eriostomum germanicum</i> Hoff. et Link		
ssp. <i>lusitanicum</i> (Hoff. et Link) G. Costa	f	—
<i>Galeopsis pyrenaica</i> Bartl.	f	1 spot
<i>G. segetum</i> Necker	f	—
<i>G. tetrahit</i> L.	f	—
<i>G. tetrahit</i> L.	l	harp, galiridoside + several o
<i>G. versicolor</i> Curt.	f	—
<i>Lallemantia peltata</i> Fisch. et Mey.	f	—
<i>Lamium album</i> L.	l, f	—
<i>L. amplexicaule</i> L.	f	lam + ac lam + 1 o
<i>L. galeobdolon</i> (L.) L.	f	1 spot
<i>L. garganicum</i> L.	f	—
<i>L. maculatum</i> L.	l	1 spot
<i>L. orvala</i> L.	l, f	lam + ac lam + 2 o
<i>L. purpureum</i> L.	f	—
<i>Leonotis leonurus</i> R.Br.	f	—
<i>L. nepetifolia</i> (L.) R.Br.	l, f	—
<i>Leonurus cardiaca</i> L. var. <i>villosus</i> (Desf.) Benth.	l, f	3 spots
<i>L. marrubiastrum</i> L.	f	—
<i>L. sibiricus</i> L.	l, f	—
<i>Leucas martinicensis</i> R.Br.	f	harp
<i>L. martinicensis</i> R.Br.	l	—
<i>L. zeylanica</i> R.Br.	l	—
<i>Melittis melissophyllum</i> L.	f	harp + ac harp + mel + monomel
<i>Molucella laevis</i> L.	f	—
<i>M. laevis</i> L.	l	ac harp + 1 o
<i>Phlomis cashmeriana</i> Royle	l	—
<i>P. fruticosa</i> L.	l	—
<i>P. fruticosa</i> L.	f	Phl. A + B
<i>P. herba-venti</i> L.	l	Phl. B
<i>P. herba-venti</i> L.	f	Phl. A + B
<i>P. pungens</i> Willd.	l	Phl. B
<i>P. pungens</i> Willd.	f	Phl. A + B
<i>P. samia</i> L.	l	Phl. B
<i>P. tuberosa</i> L.	l	—
<i>P. umbrosa</i> Turcz.	l	—
<i>Physostegia parviflora</i> Nutt.	f	1 spot
<i>P. virginiana</i> Benth.	f	1 spot
<i>P. virginiana</i> Benth.	l	Phys. A + B + C
<i>Prunella grandiflora</i> Jacq.	l	—
<i>P. laciniata</i> (L.) L.	f	—
<i>P. vulgaris</i> L.	f	—
<i>P. × webbiana</i> Paul	f	—
<i>Stachys annua</i> L.	l	1 spot
<i>S. grandiflora</i> Benth.	f	harp + 1 o
<i>S. hirta</i> L.	f	harp + 1 o

	Organ	Spots
<i>S. officinalis</i> L.	f	mel + 1 o
<i>S. palustris</i> L.	l	harp + ac harp + 1 o
<i>S. recta</i> L.	f	harp + mel + 1 o
SCUTELLARIOIDEAE		
<i>Salazaria mexicana</i> Torr.	f	cat
<i>Scutellaria albida</i> L.	l, f	cat + cat ester
<i>S. alpina</i> L.	l, f	-
<i>S. altissima</i> L.	l, f	cat + cat ester
<i>S. baicalensis</i> Georgi	l, f	-
<i>S. chitrovoi</i> Juzep.	f	-
<i>S. columnae</i> All.	l, f	cat
<i>S. costaricana</i> H. Wendl.	l	-
<i>S. galericulata</i> L.	l, f	cat
<i>S. hastifolia</i> L.	l	cat (weak)
<i>S. lateriflora</i> L.	l	cat
<i>S. minor</i> Huds.	l	cat + 1 o
<i>S. orientalis</i> L.	l	-
<i>S. oxyphylla</i> Juzep.	l	-
<i>S. parvula</i> Michx.	l, f	-
<i>S. pinnatifida</i> A. Ham.	l	-
<i>S. polyodon</i> Juzep.	l	-
<i>S. pontica</i> C. Koch	l, f	-
<i>S. scordifolia</i> Fisch.	l	cat
<i>S. siphocampyloides</i> Vatke	f	-
<i>S. sosnowskyi</i> Takht.	l	-
<i>S. taurica</i> Juzep.	l	-
<i>S. tournefortii</i> Benth.	l, f	cat + cat ester
<i>S. utriculata</i> Labill.	l, f	cat + cat ester
<i>S. ventenatii</i> Hosk.	l	-
<i>S. versicolor</i> Nutt.	l	cat + cat ester
<i>S. violacea</i> Wall.	l	-
<i>S. woronowii</i> Juzep.	l, f	cat + cat ester

- harp = harpagide
 ac harp = acetylharpagide
 mel = melittoside
 monomel = monomelittoside
 lam = lamiol
 ac lam = acetyllamiol
 cat = catalpol
 cat ester = ester of catalpol
 Phl. A = Phlomis glycoside A
 Phys. A = Physostegia glycoside A
 + 1 o = and one other spot
 l = vegetative parts
 f = fruits

biatae (except catalpol and probably the Phlomis glycosides) has as yet been found in any other family. Catalpol occurs in many families of the Tubiflorae and in the Plantaginaceae and is often in the company of aucuboside. Where it occurs in the Labiatae (*Scutellaria*, *Hemiandra*) aucuboside is absent; this situation also prevails in several Bignoniaceae, the Martyniaceae, and the Myoporaceae. Glycosides which are probably identical or chemically related to the Phlomis glycosides have been found in *Duranta* (Verbenaceae) and in *Hebenstreitia* (Scrophulariaceae) (KOOIMAN 1970, paper chromatographic evidence).

On the other hand, relatively widely occurring iridoid glycosides such as aucuboside, asperuloside, and loganoside have not been found in the Labiatae.

Within the genus *Scutellaria* a correlation was seen between the occurrence of catalpol and the subdivision of the genus given by BRIQUET (1895). *Scutellaria* is subdivided into two sections: *Scutellaria*, which contains the bulk of the species, and *Scutellariopsis*, containing only a few species, none of which were available in the present study. The first section is subdivided into three series. No catalpol was found in the series *Lupulinaria* (5 species tested) and *Heteranthesis* (3 species tested). The series *Vulgares* contains the species with catalpol, but also species which do not contain this glycoside. Catalpol was found in 6 out of 7 species tested of the subseries *Peregrinae*, in 4 species of the *Galericulatae* (but not in 4 other species), and in the sole species available of the *Lateriflorae*. Catalpol was not present in the only species tested of each of the subseries *Salviaefoliae* and *Angustifoliae*. The results of a study of the occurrence of catalpol in more species might be helpful for a future reconsideration of the subdivision of *Scutellaria*.

In the Labiatae iridoid glycosides occur in many species of the subfamilies *Prostantheroideae*, *Ajugoideae*, *Prasioideae*, *Scutellarioideae*, and of the tribes *Marrubieae* and *Stachydeae* (subfamily *Stachydoideae*). All these taxa have in common that their pollen grains are binucleate when shed. The latter character is linked with the character tricolpate pollen grains (ERDTMAN 1945; WUNDERLICH 1967). Iridoid glycosides have not been found in the subfamilies *Rosmarinoideae*, *Ocimoideae*, *Lavanduloideae*, nor in eight tribes of the *Stachydoideae*. Except for the tribe *Pogostemoneae* (*Stachydoideae*) all these taxa belong to the part of the Labiatae characterized by trinucleate and hexacolpate pollen grains. This break in the family is emphasized by the differentiation patterns of seed development and of mature seed anatomy (WUNDERLICH 1967).

It is interesting that EL-GAZZAR & WATSON (1968, 1970a), apart from their findings and proposals regarding the Verbenaceae, propose an arrangement of the Labiatae based on computational analyses of extensive comparative anatomical and morphological observations (among which actually the above-mentioned pollen grain characters). This arrangement recognizes two main groups of Labiatae and these comprise the same taxa as the groups Wunderlich arrived at. Moreover, EL-GAZZAR & WATSON (1968, 1970b) found additional material supporting the breaking-up of the family into two main groups. The trinucleate group (B) is rich in essential oils, the binucleate (A) poor (except *Pogostemon* and *Prostanthera*). Again, group B is susceptible to the rust *Puccinia*

menthae, while records for attack by the rust on members of group A are lacking in the literature (except for *Melittis*).

Finally a correlation has been found between the contents of linolenic acid of the fatty oils from seeds of the Labiatae and the phylogenetic position of the species. A high content of linolenic acid was correlated with the trinucleate group B species, a low content with the binucleate species of group A (NOVITSKAYA & KRISHTOPA 1971).

The presence of iridoid glycosides in many species of group A and their absence from group B are in accordance with these correlations. The weight of the evidence in favour of a breaking-up of the family into two main groups is therefore heavy. The absence of iridoid glycosides from group B does not mean that other iridoid compounds are absent from this group. It is well known that *Nepeta* species contain mixtures of nepeta-lactones (MC ELVAIN *et al.* 1941; SAKAN *et al.* 1965).

Within the Labiatae the taxa of group A are phylogenetically more primitive, those of group B being the most advanced. This ensues from pollen characters, seed development and seed structure (WUNDERLICH 1967) and from floral morphology (HILLSON 1959). Since group A (except the *Pogostemoneae*) is rich in iridoid glycosides and group B is devoid of these compounds, the advanced Labiatae either seem to have lost the capacity of synthesizing iridoid glycosides in the course of evolution, or to have emerged from group A-type species lacking these compounds. It is remarkable that in group B nepeta-lactones occur (so far exclusively in *Nepeta*), which are, chemically spoken, simpler compounds than the iridoid glycosides. So far it is not clear whether or not the biosynthesis of the nepeta-lactones proceeds along a simpler pathway than that of the iridoid glycosides. Probably both groups of compounds are formed via the mevalonate pathway (MEINWALD *et al.* 1966; INOUE 1971). On the other hand it is by no means surprising that it is the more primitive group of Labiatae which is rich in iridoid glycosides, since several closely related families are well-known for the occurrence of such compounds (e.g. the Verbenaceae and Scrophulariaceae). This suggests strongly that iridoid glycosides were present in the ancestors these families have in common.

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