Rastitelnye Resursy. 53(2): 163–195, 2017

SKELETON TYPES OF DITERPENOIDS AND THE SYSTEM OF GENUS *EUPHORBIA* (EUPHORBIACEAE)

© *A. L. Shavarda*,[*] *D. V. Geltman*[**]

Komarov Botanical Institute of the Russian Akademy of Science, St. Petersburg, Russia

[*] E-mail: shavarda@binran.ru

[**] E-mail: geltman@binran.ru

SUMMARY

Genus *Euphorbia* L. (Euphorbiaceae) is one of the largest genera of flowering plants and contains about 2 000 species. Recently its new system based on molecular phylogenetic approach was proposed and 4 subgenera were separated. For every subgenus new systems based on molecular data were proposed as well.

The aim of this review is to trace possible correlations between data of diterpenoids found in *Euphorbia* with new systems of the genus and its subgenera. About 170 papers on diterpenoid photochemistry of *Euphorbia* were taken into account.

General phytochemical scrutiny of *Euphorbia*

More or less representative phytochemical data are available for *Euphorbia* subgen. *Esula*. Some data are known for *Euphorbia* subgen. *Euphorbia*, but data available on subgenera *Athymalus* and *Chamaesyce* are less than fragmentary (table 1). Statistics on classes of compounds found in *Euphorbia* (table 2, fig. 1) shows the significant presence of diterpenoids in this genus — about half of the total number of known compounds.

General characteristics of terpene compounds

The basic feature of iterpenoid biogenesis is the universal mechanism of cyclization of their precursor — polyisoprenoid, activated by pyrophosphate group. Such cycloisomerization of the carbocation is widely distributed. Phosphorylated polyisopentyl precursor captures superenzymatic complex of terpensyntases and, as a result, a great number of terpenoids is formed. First of all, they differ by the number of initial structural elements (e. g. mono-, sesqui-, di-, sester- and triterpens) and also by the surprising diversity of the carbon skeleton.

Diterpenoids in genus *Euphorbia*

Analysis of available data showed the presence of 26 types of diterpene carbon skeletons in *Euphorbia*. They are divided into two classes of polycyclic and macrocyclic diterpenes (table 3). The former includes relatively common compounds similar to gibberellins: pimaranes, abietanes, atisanes, *ent*-kauranes, rosanes, cycloabietanes and erythroxylanes. The latter contains macrocyclic diterpenes and their derivatives (18 skeleton types) which often define taxonomic peculiarity on the species level.

Formal scheme of biogenetic relations of diterpene skeleton types found in *Euphorbia* is shown in fig. 2. However it does not reflect real way of diterpene biosynthesis which is poorly known. This is rather formal scheme of relationships between structural types based on minimum operating principle, i. e. when mutual transitions are characterized by minimal changes necessary for the transition from one type of carbon skeleton to another.

Data on availability of every carbon skeleton type compound in *Euphorbia* species are provided with necessary references.

Distribution of diterpene skeleton types in *Euphorbia*

In *Euphorbia* subgen. *Athymalus* diterpenes are not found yet, and in *Euphorbia* subgen. *Chamaesyce* they are currently known in section *Anisophyllum* only. Highest diversity of diterpene skeleton types within subgenus *Euphorbia* is found in section *Euphorbia*. Besides macrocyclic diterpenes lathyranes, tiglianes and ingenans common for the whole genus, daphnane skeleton (absent in subgenus *Esula*) was found in subgenus *Euphorbia*.

Data on the present diterpene skeleton types are compared with phylogenetic tree of *Euphorbia* subgen. *Esula* (fig. 5). Most sections of this subgenus possess jatrophane diterpene skeleton with great diversity of compounds; the highest number of them is found in section *Helioscopia*. However, jatrophanes are absent in sections *Myrsiniteae* and *Pithyusa* (forming highly supported clade in phylogenetic tree) as well as in sections *Lathyris*, *Exiguae* and *Chylogala*. Lathyrane skeleton is also common, although is not found in sections *Exiguae, Aphyllis*, *Pachycladae*, *Guyonianae* and *Herpetorrhizae* yet; maximum diversity of compounds of this type is identified in section *Euphorbia* (subgenus *Euphorbia*). High diversity of tigliane compounds is found in sections *Holophyllum*, *Helioscopia*, *Myrsiniteae* and *Pithyusa* and also (but with lesser diversity) in sections *Aphyllis*, *Guyonianae* and *Pachycladae*.

For some sections unique processes leading to formation of myrsinane, premyrsinane, cyclomyrsinane and ingenane skeleton types are characteristic. Compounds of myrsinane type are most diverse in section *Pithyusa*, and ingenane ones found in nearly half of sections of subgen. *Esula*. Premyrsinanes (closely related to myrsinanes) are found in sections *Myrsinites* and *Pithyusa*. It is very significant that cyclomyrsinanes are present both in perennial species of section *Pithyusa* and in annual *E. falcata*, which was only recently included into this section according to molecular studies.

The special characteristics of section *Paralias* are the presence of segetanes, presegatanes, pepluanes, paralianes and ethyl-jatrophanese. Papralians and pepluans are found also in section *Tithymalus* forming the clade together with section *Paralias*.

Sections *Holophyllum* and *Helioscopia* forming definite clade are characterized by the greatest diversity of diterpenes. Kasbanes are found only in these sections, and rhamnopholanes — in section Holophyllum only. The presence of premyrsinanes markes sections *Myrsiniteae* and *Pithyusa*, and paralianes and pepluanes — sections *Paralias* and *Tithymalus*, forming highly supported clades. However, basal monotypic section *Lathyris* which differs significantly from the others by several morphological characters, did not show any substantial difference in the set of diterpene skeleton types.

Conclusion

Our data suggest some correlation between the distribution of diterpene carbon skeleton types and the system of *Euphorbia*, especially its subgenus *Esula*. However, such correlation is not very strong, we can rather admit the existence of some tendencies. Though, there is no doubt that molecular phylogenetic data could be of use in phytochemical research including the search for particular compounds in plant species.

It is important that ingenanes and myrsinanes found in *Euphorbia* are only formally connected with lathyranes — structures inherited from possible common ancestors. The great diversity of these compounds (as well as ingenans) in basal section *Lathyris* confirms this speculation. It is likely that initially the effective cyclization of lathyrane skeleton with rearrangement took place; this process led to appearance of ingenans. The next stage of evolution led to replacement of jatrophane biogenesis by the premyrsinane cyclization mechanism which

resulted in development of sections *Holophyllum*, *Helioscopia*, *Myrsiniteae* and *Pithyusa*. The possible prototype of such process — tigliane cyclozation of lathyranes existed in other Euphorbiaceae and was found in basal clade of *Euphorbia* subgen. *Esula*.

Key words: *Euphorbia*, diterpenoids, carbon skeleton.