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Diterpenoids in the Essential Oils from the Genus *Stachys*

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Abstract: The occurrence of diterpenoids in the essential oils of the species of the genus *Stachys* (Lamiaceae, Labiatae) is reviewed.

Keywords: Diterpenoids; Lamiaceae; *Stachys;* essential oils.

The genus *Stachys* is one of the largest representative genera of the Lamiaceae (Labiatae) family, and includes about 300 species [1-4], in the subtropical and tropical regions of both hemispheres.

A large number of essential oils were obtained by hydrodistillation of species of *Stachys*. The investigations on the chemical composition of these oils were strongly expanded in the last ten years by developed GC-MS analysis techniques. Obviously monoterpenoids and sesquiterpenoids are the prevailing constituents. However, in some oils the occurrence of diterpenoids was observed as quite minor constituents or traces; usually these products were merely identified but not isolated.

The present review aims to collect data on their occurrence, usually difficult to be extrapolated from the single original papers. Most of the works were contributed by researchers from Greece, Turkey, Iran and Balkanic countries.

In this review we report papers in which the occurrence of diterpenoids was observed. The apparent absence of diterpenoids in several species can depend on their occurrence in so small traces or on the sensitivity of the instruments used for the analysis.

The diterpenoids identified in each species are reported in Table 1, quoting for the same species the contributions of more researchers whereas in Table 2 the diterpenoids are listed with species in which they occur. In total, forty-five diterpenoids were detected, showing different skeleta (e.g. labdane, abietane, kaurane, pimarane) from thirty species and subspecies of *Stachys*.

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Table 1. Diterpenic content of the taxa of *Stachys*.

Taxa	Compounds
alopecurus	13*R*,*S*-14,15-dinorlabdane-8,13-diol [5], manoyl oxide 13-*epi* [5], labda-13(16),14-dien-8-ol [5]
alpina dinarica	phytol [6]
balansae	kaur-16-ene [7], cembrene [8]
byzantina	cembrene [9], phytol [9], manoyl oxide [9], manoyl oxide 13-*epi* [9], 3α-hydroxy-manool [9]
candida	manoyl oxide [10], abietatriene [10], manool [10], dehydroabietol 4-*epi* [10]
chrysantha	manoyloxide [10], abietatriene [10], manool [10], dehydroabietal [10], dehydroabietol 4-epi [10]
cretica cretica	pimaradiene [5], isophyllocladene [5]
germanica	manool 13-*epi* [11], laurenene *epi* [12][20], abietatriene [13]
germanica heldreichii	isophyllocladene [5], manoyl oxide 13-*epi* [5], phytol *trans* [5]
glutinosa	cleroda-2,4(18),14-trien-13-ol [14], isopimara-8,15-diene [15], manoyl oxide [15], abietatriene [15], cleroda-3,14-dien-13-ol [15], laurenene *epi* [16], isopimara-9(11),15-diene [16], sclarene [16]
iberica stenostachya	phytol [17]
inflata	phytol [9]
ionica	sclarene [18], manoyl oxide [18], manoyl oxide 13-*epi* [18], abietatriene [18], sclareol [18]
laetivirens	8,13-epoxy-15,16-dinor-labd-12-ene [19], kaur-16-ene [19], phytol [19]
lavandulifolia	manoyl oxide [9], manoyl oxide 13-*epi* [9], phytol acetate [9], phytol [20]
laxa	phytol [9]
menthifolia	manool 13-*epi* [5], manoyl oxide 13-*epi* [5], kaur-16-ene [5], abietatriene [5], phytol *cis* [5], 3β-hydroxy-manoyl oxide 13-*epi* [5], abieta-8,11,13-trien-7-one [5], 3β-acetoxy-manoyl oxide 13-*epi* [5], labd-13-ene-8,15-diol [5]
obtusicrena	phytol *trans* [21]
officinalis	phytol *trans* [11]
pilifera	phytol [22], manoyl oxide [22]
plumosa	pimara-8(14),15-diene *ent* [11], manool 13-*epi* [11], manoyl oxide [11][23][24][25], kaur-16-ene [11][23][24][25], abietatriene [11][23][24][25], phytol *trans* [11], abieta-7,13-dien-3-one [11], pimaradiene [23], 3(*Z*)-cembrene A [23], biformene [23], thunbergol [23], totarol *cis* [23], abieta-8,11,13-trien-7-one [23], dehydroabietol [23], isopimara-8,15-diene [24][25], manool [24]
recta	kaur-16-ene [7], phytol *cis* [5]
scardica	phytol *trans* [11]
schtschegleevii	phytol [26]
spruneri	sandaracopimara-8(14),15-diene [18], kaur-15-ene [18], manoyl oxide [18], manoyl oxide 13-*epi* [18], abietatriene [18], abietadiene [18], dehydroabietal [18], abieta-7,13-diene-3-one [18], ferruginol *trans* [18], dehydroabietol 4-*epi* [18]
sylvatica	phytol [27], manoyl oxide [28], manoyl oxide 13-*epi* [28], kaur-16-ene [28], manool [28], abietal [28], abietatriene [11], phytol *trans* [11], sclareol [11]

Table 1. continued

swainsonii argolica	cembrene [18], pimaradiene [18], *neo*-cembrene [18], sandaracopimara-8(14),15-diene [18], manoyl oxide [18], manoyl oxide 13-*epi* [18], cembra-2,7,11-trien-4-ol [18], abietatriene [18], phytol *trans* [18], dehydroabietal [18], ferruginol *trans* [18], dehydroabietol 4-*epi* [18], neoabietic acid [18]
swainsonii melangavica	phytol *trans* [18], manoyl oxide [18], manoyl oxide 13-*epi* [18], abietatriene [18], dehydroabietal [18], dehydroabietol 4-*epi* [18]
swainsonii scyronica	sclarene [18], manoyl oxide [18], abietatriene [18], phytol *trans* [18], sclareol [18], dehydroabietal [18], dehydroabietol 4-*epi* [18]
swainsonii swainsonii	isopimara-9(11),15-diene [18], manoyl oxide [18], manoyl oxide 13-*epi* [18], abietatriene [18], neoabietic acid [18]

Usually, the diterpenoids occur in very small amount or in traces. There are some exceptions: so abietatriene was found in *S. plumosa* [23][24][25] in the range 45.5%-61,2% pimaradiene 18,6 % in *S. cretica* [5], isophyllocladene 14,2 % in *S. germanica heldreichii* [5], manoyl oxide 12,07 % in *S. candida* [10], kaur-16-ene 9,0 % in *S. menthifolia* [5], cleroda-2,4(18),14-trien-13-ol 12,3 % in *S. glutinosa* [15], phytol 17,9 % in *S. laetivirens* [19].

Table 2. Occurrence of diterpenoids in the taxa of *Stachys*.

No	Compounds	Taxa
1	abietadiene	*S. spruneri* [18]
2	abieta-7,13-dien-3-one	*S. spruneri* [18], *S. plumosa* [11]
3	abietal	*S. sylvatica* [28]
4	abietatriene	*S. spruneri* [18], *S. swainsonii melangavica* [18], *S. swainsonii argolica* [18], *S. swainsonii swainsonii* [18], *S. swainsonii scyronica* [18], *S. ionica* [18], *S. sylvatica* [11], *S. menthifolia* [5], *S. plumosa* [11][23][24][25], *S. germanica* [13], *S. glutinosa* [15], *S. candida* [10], *S. chrysantha* [10]
5	abieta-8,11,13-trien-7-one	*S. menthifolia* [5], *S. plumosa* [23]
6	3β-acetoxy-13-*epi*-manoyl oxide	*S. menthifolia* [5]
7	biformene	*S. plumosa* [23]
8	cembra-2,7,11-trien-4-ol	*S. swainsonii argolica* [18]
9	cembrene	*S. balansae* [8], *S. byzantina* [9], *S. swainsonii argolica* [18]
10	3(*Z*)-cembrene A	*S. plumosa* [23]
11	cleroda-3,14-dien-13-ol	*S. glutinosa* [15]
12	cleroda-2,4(18),14-trien-13-ol	*S. glutinosa* [14]
13	dehydroabietal	*S. chrysantha* [10], *S. spruneri* [18], *S. swainsonii argolica* [18], *S. swainsonii melangavica* [18], *S. swansonii scyronica* [18]
14	dehydroabietol	*S. plumosa* [23]
15	dehydroabietol-4-*epi*	*S. candida* [10], *S. spruneri* [18], *S. chrysantha* [10], *S. swainsonii argolica* [18], *S. swainsonii melangavica* [18], *S. swainsonii scyronica* [18]
16	13*R*,*S*-14,15-dinorlabdane-8,13-diol	*S. alopecurus* [5]
17	8,13-epoxy-15,16-dinor-labd-2-ene	*S. laetivirens* [19]
18	ferruginol *trans*	*S. spruneri* [18]
19	3β-hydroxy-manoyl oxide-13-*epi*	*S. menthifolia* [5]
20	3α-hydroxy-manool	*S. byzantina* [9]

Table 2. continued

21	isophyllocladene	*S. cretica cretica* [5], *S. germanica heldreichii* [5]
22	isopimara-8,15-diene	*S. glutinosa* [15], *S. plumosa* [24][25]
23	isopimara-9(11),15-diene	*S. swainsonii swainsonii* [18], *S. glutinosa* [16]
24	kaur-15-ene	*S. spruneri* [18]
25	kaur-16-ene	*S. menthifolia* [5], *S. plumosa* [11][23][24][25], *S. recta* [7], *S. sylvatica* [28], *S. laetivirens* [19], *S. balansae* [7]
26	labd-13-en-8,15-diol	*S. menthifolia* [5]
27	labda-13(16),14-dien-8-ol	*S. alopecurus* [5]
28	laurenene *epi*	*S. glutinosa* [16], *S. germanica* [12]
29	manool	*S. candida* [10], *S. chrysantha* [10], *S. sylvatica* [28], *S. plumosa* [24]
30	manool-13-*epi*	*S. germanica* [11], *S. menthifolia* [5], *S. plumosa* [11]
31	manoyl oxide	*S. byzantina* [9], *S. candida* [10], *S. chrysantha* [10], *S. glutinosa* [15], *S. ionica* [18], *S. lavandulifolia* [9], *S. pilifera* [22], *S. plumosa* [11][23][24][25], *S. spruneri* [18], *S. sylvatica* [28], *S. swainsonii argolica* [18], *S. swainsonii melangavica* [18], *S. swainsonii scyronica* [18], *S. swainsonii swainsonii* [18]
32	manoyl oxide-13-*epi*	*S. alopecuros* [5], *S. byzantina* [9], *S. germanica heldreichii* [5], *S. ionica* [18], *S. lavandulifolia* [9], *S. menthifolia* [5], *S. spruneri* [18], *S. sylvatica* [28], *S. swainsonii argolica* [18], *S. swainsonii melangavica* [18], *S. swainsonia swainsonii* [18]
33	neoabietic acid	*S. swainsonii argolica* [18], *S. swainsonii swainsonii* [18]
34	*neo*-cembrene (cembrene A)	*S. swainsonii argolica* [18]
35	phytol	*S. alpina dinarica* [6], *S. byzantina* [9], *S. iberica stenostachya* [17], *S. inflata* [9], *S. laetivirens* [19], *S. lavandulifolia* [20], *S. laxa* [9], *S. pilifera* [22], *S. schtschegleevii* [26], *S. sylvatica* [27]
36	phytol *trans*	*S. obtusicrena* [21], *S. officinalis* [11], *S. plumosa* [11], *S. scardica* [11], *S. sylvatica* [11], *S. swainsonii argolica* [18], *S. swainsonii melangavica* [18], *S. swainsonii scyronica* [18], *S. germanica heldreichii* [5]
37	phytol *cis*	*S. menthifolia* [5], *S. recta* [5]
38	phytol acetate	*S. lavandulifolia* [9]
39	pimaradiene	*S. cretica cretica* [5], *S. plumosa* [23], *S. swainsonii argolica* [18]
40	pimara-8(14),15-diene *ent*	*S. plumosa* [11]
41	sandaracopimara-8(14),15-diene	*S. swainsonii argolica* [18]
42	sclarene	*S. glutinosa* [16], *S. ionica* [18], *S. swainsonii scyronica* [18]
43	sclareol	*S. ionica* [18], *S. sylvatica* [11], *S. swainsonii scyronica* [18]
44	thunbergol	*S. plumosa* [23]
45	totarol *cis*	*S. plumosa* [23]

References

[1] J.C. Willis (1966). "A Dictionary of the flowering plants and ferns", 7th edition, Cambridge University Press, Cambridge UK.

[2] K.H. Rechinger and I.C. Hedge (1982). "Flora Iranica" vol. 150, AkademischeDruck Verlagsanstalt, Graz Austria.

[3] W. Greuter, H.M. Burdet and G. Long (1986). "Med-Check List" vol. 3, Ed. Conserv. Jardin Botan. Genéve Switzerland.

[4] D.J. Mabberley (1997). "The Plant Book" 2nd edition, Cambridge University Press, Cambridge UK.

[5] H.D. Skaltsa, C. Demetzos, D. Lazari and M. Sokovic (2003). Essential oil analysis and antimicrobial activity of eight *Stachys* species from Greece, *Phytochemistry* **64**, 743-752.

[6] J. Kukic, S. Petrovic, M. Pavlovic, M. Couladis, O. Tzakou and M. Niketic (2006). Composition of essential oil of *Stachys alpina* L. ssp. *dinarica* Murb, *Flavour Fragr. J.* **21**, 539-542.

[7] A. Cakir, M.E. Duru, M. Harmandar, S. Izumi and T. Hirata (1997). The volatile constituents of *Stachys recta* L. and *Stachys balansae* L. from Turkey, *Flavour Frag. J.* **12**, 215-218.

[8] S. Rezazadeh, M.P. Hamedani, R. Dowlatabadi, D. Yazdani and A. Shafiee (2006). Chemical composition of the essential oils of *Stachys schtschegleevii* Sosn. and *Stachys balansae* Boiss. et Kotschy from Iran, *Flavour Fragr. J.* **21**, 290-293.

[9] K. Morteza-Semnani, M. Akbarzadeh and S. Changizi (2006). Essential oils composition of *Stachys byzantina*, *S.inflata*, *S.lavandulifolia* and *S.laxa* from Iran, *Flavour Fragr. J.* **21**, 300-303.

[10] H.D. Skaltsa, D.M. Lazari, I.B. Chinou and A.E. Loukis (1999). Composition and antibacterial activity of the essential oils of *Stachys candida* and *S. chrysantha* from Southern Greece, *Planta Med.* **65**, 255-256.

[11] S. Grujic-Jovanovic, H.D. Skaltsa, P. Marin and M. Socovic (2004). Composition and antibacterial activity of the essential oil of six *Stachys* species from Serbia, *Flavour Fragr. J.* **19**, 139-144.

[12] E. Haznagy-Radnai, Sz. Cziglee and I. Màthé (2007). Analysis of the essential oil of downy woundwort (*Stachys germanica* L.), *Acta Facult. Pharm. Univ. Comenianae* **54**, 78-83.

[13] S. Grujic-Jovanovic, P.D. Marin, A. Dzamic and M. Ristic (2008) Composition of the essential oil of *Stachys germanica* from Serbia, *Chem. Nat. Comp.* **44**, 670-672.

[14] J.P. Mariotti, F. Tomi, A.F. Bernardini, J. Costa and J. Casanova (1996). Chemical composition of essential oils of *Stachys glutinosa* from Corsica and Sardinia, *Rivista Italiana EPPOS* **7**, 536-541.

[15] J.P. Mariotti, J. Costa, A. Bianchini, A.F. Bernardini and J. Casanova (1997). Composition and variability of the essential oil of *Stachys glutinosa* L. from Corsica (France), *Flavour Fragr. J.* **12**, 205-209.

[16] G. Pintore, M. Chessa, P. Manconi, S. Zanetti, A. Deriu and B. Tirillini (2006). Chemical composition and antimicrobial activities of essential oil of *Stachys glutinosa* from Sardinia, *Nat. Prod. Commun.* **1**, 1133-1136.

[17] A. Kaya, B. Demirci and K.H.C. Baser (2001). The composition of the essential oil of *Stachys iberica* subsp. *stenostachya* growing in Turkey, *Chem. Nat. Comp.* **37**, 326-328.

[18] H.D. Skaltsa, A. Mavrommati and T. Constantinidis (2001). A chemotaxonomic investigation of volatile constituents in *Stachys* subsect. Swainsonianeae (Labiatae), *Phytochemistry* **57**, 235-244.

[19] H. Duman, M. Kartal, L. Altun, B. Demirci and K.H.C. Baser (2005). The essential oil of *Stachys laetivirens* Kotschy et Boiss. ex Rech. fil., endemic in Turkey, *Flavour Fragr. J.* **20**, 48-50.

[20] M.H. Meshkatalsadat, E. Sajjadi and H. Amiri (2007). Chemical constituents of the essential oils of different stages of the growth of *Stachys lavandulifolia* Vahl. from Iran, *Pakistan J. Biol. Sci.* **10**, 2784-2786.

[21] K. Javidnia, H. Rezai, R. Miri and A. Jafari (2006). Composition of the essential oil of *Stachys obtusicrena* Bois. from Iran, *J. Essent. Oil Res.* **18**, 146-148.

[22] K. Javidnia, R. Miri, M.R. Moein, M. Kamalinejad and H. Sarkazadeh (2006). Constituents of the essential oil of *Stachys pilifera* Benth. from Iran, *J. Essent. Oil Res.* **18**, 275-277.

[23] S. Petrovic, M. Ristic, M. Milenkovic, J. Kukic, J. Antic-Stankovic and M. Niketic (2006). Composition and antimicrobial activity of essential oil of *Stachys plumosa* Griseb, *Flavour Fragr. J.* **21**, 250-252.

[24] N. Radulovic, J. Lazarevic, N. Ristic and R. Palic (2007). Chemotaxonomic significance of the volatiles in the genus *Stachys* (Lamiceae): Essential oil composition of four Balkan *Stachys* species, *Biochem. System. Ecol.* **35**, 196-208.

[25] N. Ristic, J. Lazarevic, N. Radulovic and R. Palic (2008). Antimicrobial activity of the essential oils of selected *Stachys* species, *Chem. Nat. Comp.* **44**, 522-525.
[26] H. Norouzi-Arasi, I. Yavari and M. Alibabaeii (2004). Chemical constituents of the essential oil of *Stachys schtschegleevii* Sosn. from Iran, *J. Essent. Oil Res.* **16**, 231-232.
[27] B. Tirillini, R. Pellegrino and L. Maleci Bini (2004). Essential oil composition of *Stachys sylvatica* L. from Italy, *Flavour Fragr. J.* **19**, 330-332.
[28] E. Radnai, A. Dobos, K. Veres, L. Tòth, I. Mathé, G. Janicsak and G. Blunden (2003). Essential oils in some *Stachys* species growing in Hungary, *Acta Hort*. **597**, 137-142.