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The chemical constituents of new essential oils from endemic and sub endemic plants of Mongolian Gobi

S. Shatar, J. Staneva, M. Todorova & Sh. Altantsetseg

Abstract

The new essential oil-Endemic and sub endemic plants in Outer Mongolian Gobi were isolated by hydro distillation from the aerial parts of *Brachanthemum gobicum* Krasch, *B. mongolicum* Krach, *B. mongolorum* Grub., *Asterothamnus centrali-asiaticus* Novopork, *A. molliusculus* Novopork., *Ajania trifida* (Turcz) Tzvel, *A. achilleoides* (Turcz) Tzvel., *Ferula ferulaeoides* (Stend) Eug.Kor., *Artemisia davajamczii* Darijima., *A. caespitosa* Ldb, *A. subchrysolepis* Filat, *A. schischkinii* Krasch, *A. intricata* Franch, *A. ordosica* Krasch, *A. gobica* (Krasch) Grub., *A. sphalerocephala* Krasch that grown in wild in Outer Mongolian Gobi. The essential oils were analyzed by a combination of Capillary GC and GC-MS and their main constituents were described.

Key words: Mongolian Gobi, endemic, subendemic plant species, essential oils, main constituents

Introduction

The genus *Artemisia* (family Compositae, tribe Anthemideae) which contains many useful aromatic and medicinal plants, comprises of about 400 species found in the northern hemisphere (MARCO & BARBERA 1990). It presents 103-106 species that are found in the wild all over in Outer Mongolia (GRUBOV 1982, GUBANOV 1996, DARIJIMAA 2003). This genus is of a great interest for food, medicine, perfume and cosmetics industries because some of its species containing valuable volatile oils (GORYAEV et al. 1962, BEREZOVSKAYA et al. 1991, SHATAR 1998).

Many *Artemisia* species have a characteristic scent or taste, based on monoterpenes, sesquiterpenes and sesquiterpen lactons, which is one reason why they are often applied in folk medicine (SHATAR 2011, SHATAR & ALTANTSETSEG 2011). *Artemisia* spp. are globally used in tonic, stomachic and stimulant beverages and as antiphlogistics in antiseptic oils or tinctures applied for the relief of rheumatic pains PARIS & MOISE 1971, SHATAR 1989). They are also raw material of fragrances, perfumery and in cosmetic products (LAWRENCE 1982, 1990). The leaves are used in Mongolian traditional medicine to relieve gastroenteritis, dysentery, diarrhea, and they have antimicrobial and antinociceptive activity (SHATAR 1989, 1998, 2011; SHATAR & ALTANTSETSEG 2011). 1.8-cineole and camphor, which are the most important component of the essential oils of *Artemisia*, have strong anticeptic properties (COWAN 1999, LAWRENCE 1982,1990; SHATAR 1998, SHATAR & ALTANTSETSEG 2011).

The aim of this paper was to investigate the chemical composition of the essential oils of endemic and sub-endemic *Compositae* of Mongolia, including several *Artemisia* spp. and related genera plus one *Apiaceae* included for comparison: *Brachanthemum gobicum* Krasch, *B. mongolicum* Krach, *B. mongolorum* Grub., *Asterothamnus centrali-asiaticus* Novopork, *A. molliusculus* Novopork., *Ajania trifida* (Turcz) Tzvel, *A. achilleoides* (Turcz) Poljak., *Artemisia davajamczii* Darijima., *A. caespitosa* Ldb, *A. subchrysolepis* Filat, *A. schischkinii* Krasch, *A. intricata* Franch, *A. ordosica* Krasch, *A. gobica* (Krasch) Grub, *A. sphalerocephala* Krasch and *Apiaceae*: *Ferula ferulaeoides* (Steud) Eug. Kor.

Material and methods

Plant material: aromatic plants for assessment of new essential oils were collected from the Eastern Gobi and Dzungarian Gobi of Mongolia. Voucher specimens were deposited at the herbarium of the Institute of Botany of the Mongolian Academy of Science in Ulaanbaatar.

Isolation of oils: air-dried leaves and resin (200 g) were water-distilled for 2 h using a circulatory Clevenger-type apparatus (ADAMS 1991).

Analyses: oils from each species were analyzed and average values are given below. The oils were analyzed on a HP 5971 MSD mass-spectrometer with scan time of 1 sec, directly coupled to a HP 5890 gas chromatography, using a J and W DB-5, 30m x 0.26mm, 0.25 μ m coating thickness, fused silica capillary column. The column was programmed from 60-240 $^{\circ}$ C at 3 $^{\circ}$ C/min. Oils were identified based on library searches of the (authors) volatile oil library (ADAMS 2006), using the HP chem. Station library search routines, coupled with retention time data of authentic reference compounds.

Quantity was assessed by FID (flame ionization detector) on an HP 5890 gas chromatography using a J and W DB-5, 0.26mm x 30m, 0.25 micron coating thickness, fused silica capillary column, programmed under the same conditions as above using the HP chem. station software.

Results and discussion

The genus *Brachanthemum* DC

(GRUBOV 1982, GUBANOV 1996, SHATAR 1998, SHATAR & ALTANTSETSEG 2011)

Previous work: No previous studies were found for any of these species.

Present work: The clear essential oil of *Brachanthemum gobicum* (from two sites in the Gobi-Desert) was dominated by 1.8-cineole (39.1 %, 42.6 %) and camphor (27.4 %, 29.1 %) with moderate amounts of camphene (3.4 %, 6.1 %) α -pinene (1.4 %, 2.5 %) p-cymene (3.4 %, 1.8 %) terpinen-4-ol (2.5 %, 1.8 %) and cis-sabinene hydrate (0.5 %, 1.3 %).

The oil of *B. mongolicum* was clear and similar to *B. gobicum* in having an abundance of camphor (39.5 %) and 1.8-cineole (20.2 %) with moderate amounts of camphene (11.5 %) α -pinene (1.3 %) and p-cymene (1.1 %). However, *B. mongolicum* differed from *B. gobicum* in having only moderate amounts of borneol (9.5%), bornylacetate (4.1 %), α -thujone (1.9 %) and β -thujone (0.5 %) cis-chrysanthenyl acetate (0.5 %) and camphor which is the most important component of the oil of both *Brachanthemum* and *Artemisia* and has strong antiseptic properties.

The major constituent of blue oil of *B. mongolorum* was chamazulene (18.3 %) giving the oil its bright blue color. The second major constituents of the oil were 1.8-cineole (14.6 %), camphor (10.0 %) followed by β -caryophyllene (7.2 %), germacrene-D (5.4 %), dehydro-1.8-cineole (4.5 %), p-cymene (3.8 %), (E)- β -ocimene (3.6 %), caryophyllene oxide (2.7 %) and limonene (2.3 %). It is noteworthy that the oil of *B. mongolorum* was rich in many minor sesquiterpenes not found in either *B. gobicum* or *B. mongolicum*. (see table 1).

The genus *Asterothamnus* Novopork

(GRUBOV 1982, GUBANOV 1996, SHATAR 1998, SHATAR & ALTANTSETSEG 2011)

Previous work: No previous studies were found for any of these species (SHATAR 1989).

Present work: The essential oils of *A. centrali-asiaticus* corresponded to only 0.2-0.3 % (w/w) based on dry material: monoterpene hydrocarbons (63.5-91.2 %), oxygenated monoterpenoids, sesquiterpene hydrocarbons (4.3 %) and oxygenated sesquiterpenoids (5.4 %). The main constituents were β -pinene (11.6 %, 31.4 %), sabinene (22.0 %, 9.8 %), (Z)- β -ocimene (5.0 %, 8.9 %), β -phellandrene (5.3 %, 7.6 %), terpin-4-ol (0.8 %, 7.1 %), terpinolene (5.1 %, 6.2 %), α -pinene (3.7 %, 5.3 %), spathulenol (4.8 %, 0.1 %), myrcene (2.9 %, 3.4 %), γ -terpinene (0.8 %, 2.6 %), α -phellandrene (1.0 %, 2.7 %), bicycle germacrene (0.9 %, 2.1 %), camphene (0.6 %, 1.8 %), limonene (1.2 %, 1.5 %), α -terpinene (1.0 %, 1.2 %), p-cymene (0.2 %, 1.1 %) and methyleugenol (0.4 %, 0.9 %).

Table 1: Chemical constituents of the *Brachanthemum* species from Mongolian Gobi Desert (of *B. gobicum* two specimens were available)

Compounds (%)	Species of <i>Brachanthemum</i>			
	<i>B. gobicum</i>	<i>B. mongolicum</i>	<i>B. mongolorum</i>	
α-pinene	1.4	2.5	1.3	0.6
camphene	3.4	6.1	11.5	1.3
β-pinene	0.7	1.2	0.8	0.7
myrcene	0.2	0.3	0.4	4.5
p-cymene	3.4	1.8	1.1	3.8
limonene	0.1	0.2	0.1	2.3
γ-terpinene	0.4	1.2	0.4	1.7
1.8-cineole	39.1	42.6	20.2	14.6
cis-sabinene hydrate	0.5	1.3	0.2	1.1
cis-thujone	-	-	1.9	-
trans-thujone	0.9	-	0.5	-
camphor	27.4	29.1	39.5	10.0
borneol	0.4	0.8	9.5	4.8
terpin-4-ol	2.5	1.8	0.6	1.4
α-terpineol	2.7	1.4	0.2	1.8
cis-chrysanthenyl acetate	0.2	-	0.5	-
bornyl acetate	-	-	4.1	-
terpinyl acetate	1.3	0.1	0.5	-
E-caryophyllene	0.2	0.1	0.1	7.2
γ-curcumene	-	-	-	1.2
germacrene-D	-	0.2	-	5.4
β-selinene	-	0.3	-	1.0
α-zingiberene	-	-	-	0.9
bicyclogermacrene	-	-	-	0.7
spathulenol	1.2	0.2	-	1.0
caryophyllene oxide	-	-	-	2.7
chamazulene	-	-	-	18.3
Monoterpene hydrocarbons	10.9	1.5	17.5	19.9
Oxygenated monoterpenoids	77.9	82.5	81.3	35.8
Sesquiterpene hydrocarbons	0.3	0.6	0.3	18.6
Oxygenated sesquiterpeneoids	1.4	0.2	-	24.3
Total	90.5	99.1	98.9	98.6

The essential oil of *A. molliusculus* consisted mainly of oxygenated monoterpenoids (52.0 %) and monoterpene hydrocarbons (47.5 %). The major constituents of the essential oil were camphor (34.9 %), β-pinene (20.8 %), sabinene (9.8 %), 1.8-cineole (9.2 %), limonene (5.0 %), α-pinene (4.9 %), β-phellandrene (3.7 %), myrcene (3.0 %), borneole (3.0 %), α-thujone (2.8 %) and terpin-4-ol (2.0 %, see table 2).

The genus *Ajania* Poljak

(GRUBOV 1982, GUBANOV 1996, SHATAR 1989, 1998; SHATAR & ALTANTSETSEG 2011)

Previous work: No previous studies were found for any of these species (SHATAR 1989).

Present work: The essential oil of *Ajania trifida* comprised oxygenated monoterpenoids (75.9 %), monoterpene hydrocarbons (13.5 %), oxygenated sesquiterpeneoids (1.3 %) and sesquiterpene hydrocarbons (0.9 %). The main constituents of the essential oil were camphor (41.2 %), 1,8-cineole (12.3 %), borneole (6.9 %), sabinene (5.9 %), α -pinene (3.1 %), p-cymene (3.0 %), terpin-4-ol (2.8 %), bornylacetate (1.4 %), myrcene (1.3 %), thymol (0.8 %), carvacrol (0.3 %).

The essential oil of *A. achilleoides* contained oxygenated monoterpenoids (86.4 %), oxygenated sesquiterpeneoids (4.4 %), monoterpene hydrocarbons (2.9 %) and sesquiterpene hydrocarbons (0.6 %). The main constituents were camphor (58.3 %), 1,8-cineole (10.4 %), borneole (5.0 %), trans-sabinol (2.7 %), terpin-4-ol (2.5 %), myrcene (2.2 %), spathulenol (1.6 %), caryophyllene oxide (1.3 %) and α -bisabolol (0.7 %); see table 2.

The genus *Artemisia* L.

(GRUBOV 1982, GUBANOV 1996, SHATAR 1989, 1998; SHATAR & ALTANTSETSEG 2011)

Previous work: No previous studies were found for any of these species (SHATAR 1989, 1998; SHATAR & ALTANTSETSEG 2011).

Present work: The essential oil of *Artemisia davajamczii* consisted of oxygenated monoterpenoids (71.53 %), other sesquiterpene and sesquiterpeneoids (23.66 %). The main components were 1,8-cineole (28.83 %), α -thujone (12.90 %), camphor (8.53 %), β -thujone (6.76 %), terpin-4-ol (3.83 %), artemisia keton (3.08 %), chrysanthenone (2.61 %), α -terpineol (1.94 %), p-cymene (1.50 %), cis-sabinenhydrate (1.41 %), trans-sabinenhydrate (1.04 %), sabinene (1.93 %), α -pinene (0.73 %) and camphene (0.69 %).

The essential oil of *A. gobica* had oxygenated monoterpenoids (67.95 %) and monoterpene hydrocarbons (7.35 %). The main components included: camphor (25.16 %), 1,8-cineole (15.30 %), α -thujone (12.80 %), β -thujone (3.70 %), artemisia alcohol (3.35 %), γ -terpinene (1.90 %), myrcene (1.60 %), p-cymene (1.40 %), sabinene (1.10 %) and camphene (0.8%).

The essential oil of *A. caespitosa* contained oxygenated monoterpenoids (64.90 %) and monoterpene hydrocarbons (4.08 %). The main compounds were 1,8-cineole (31.10 %), camphor (12.55 %), α -thujone (7.32 %), terpin-4-ol (6.83 %), trans-sabinen hydrate (1.46 %), β -thujone (1.46 %), sabinene (1.34 %), camphene (1.27 %), α -terpineol (1.26 %) and trans-piperitol (0.88 %).

The essential oil of *A. subchrysolepis* consisted of oxygenated monoterpenoids (90.40 %) and monoterpene hydrocarbons (9.41 %). The main components included camphor (35.90 %), β -thujone (20.82 %), α -thujone (14.94 %), 1,8-cineole (11.75 %), camphene (5.48 %), α -terpineol (3.80 %), myrtenol (3.42 %), terpineol (3.12 %), p-cymene (1.80 %), sabinene (1.10 %) and borneol (1.00 %).

The essential oil of *A. schischkinii* comprised oxygenated monoterpenoids (80.47 %) and monoterpene hydrocarbons (13.12 %). The main components were camphor (46.51 %), 1,8-cineole (17.11 %), α -thujone (15.40 %), camphene (4.44 %), sabinene (2.13 %), β -thujone (1.60 %), α -pinene (1.35 %), β -pinene (1.01 %), myrcene (0.69 %), chrysanthenone (0.61 %), α -terpineol (0.53 %), borneol (0.53 %), and terpin-4-ol (0.42 %).

The essential oil of *A. intricata* had a high content of oxygenated monoterpenoids (71.57 %) and monoterpene hydrocarbons (10.42 %). The main components were camphor (50.02 %), 1,8-cineole (15.38 %), camphene (5.11), terpin-4-ol (2.92 %), p-cymene (2.54 %), borneol (2.01 %), α -pinene (1.30 %), β -pinene (1.10 %) and sabinene (1.08 %).

The essential oil of *A. sphaerocephala* consisted monoterpene hydrocarbons (52.67 %), sesquiterpene hydrocarbons (15.92 %) and oxygenated monoterpenoids (15.76 %). The main components included β -pinene (16.16 %), germacrene-D (14.83 %), γ -terpinene (11.60 %), (E)- β -ocimene (8.80 %), α -pinene (5.41 %), (Z)- β -ocimene (5.10 %), myrcene (3.67 %), cis-chry-santhenyl acetate (1.82 %), methylugenol (1.66 %), sabinene (1.74 %) and cis-sabinene hydrate (1.55 %).

The essential oil of *A. ordosica* contained monoterpene hydrocarbons (75.64%) and oxygenated monoterpeneoids (7.76%). The main components were (Z)- β -ocimene (19.14%), β -pinene (18.40%), limonene (8.20%), trans-sabinen hydrate (7.76%), α -pinene (7.10%), sabinene (6.66%), p-cymene (5.74%), γ -terpinene (4.32%), (E)- β -ocimene (3.20%) and myrcene (2.88%); see table 2.

The oil of *Ferula ferulaeoides* (Steud.) Kor.

(SHATAR 1998, SHATAR & ALTANTSETSEG 2011)

Previous work: No previous studies were found for this species (SHATAR 1989).

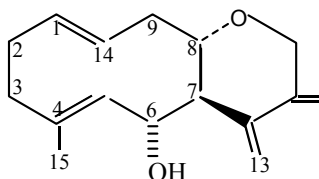
Present work: The essential oils from the leaves of *Ferula ferulaeoides* had high contents of oxygenated sesquiterpeneoids (46.7 %), oxygenated monoterpeneoids (16.2 %), sesquiterpene hydrocarbons (15.8%) and monoterpene hydrocarbons (4.2 %).

The major components of the essential oil were guaiol (18.1%), eudesmol (13.0 %), nerolidole (10.1 %), 1.8-cineole (4.4 %), myristicine (4.3 %), bornylacetate (3.4 %), β -bisabolol (2.0 %), acoradiene (1.8 %), α -pinene (1.6 %), β -bisabolene (1.5 %), daucene (1.7 %), guaiene (1.2 %) and α -himachalene (1.1 %).

The essential oil from resin of *F. ferulaeoides* contained oxygenated sesquiterpeneoids (70.7 %), sesquiterpene hydrocarbons (8.0 %), oxygenated monoterpeneoids (4.5 %), and monoterpene hydrocarbons (1.7 %). The main constituents were: guaiol (58.8 %), E-nerolidole (10.2 %), β -farnesene (3.0 %), myristicine (1.7 %), β -bisabolene (1.3 %), bornylacetate (1.2 %), bulnesol (1.0 %) and α -selinene (0.8 %); see table 3.

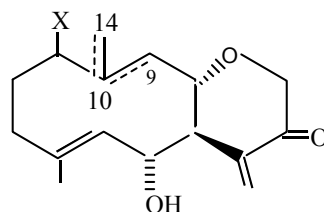
Lactone profile of *Brachanthemum gobicum* Krasch from Mongolian Gobi

Brachanthemum gobicum Krasch is endemic and yielded an essential oil which contains sesquiterpene lactones new for the Mongolian Gobi Desert (STANEVA et al. 2010). The crude sesquiterpene lactone fraction of *B. gobicum* Krasch afforded: germacranolides (1-8). Their structures are presented in fig 1.



1a.

1. 4 β ,5 α -epoxy
2. 4 α ,5 β -epoxy
3. 1 α ,10 β -epoxy
- 3a. 1 β ,10 α -epoxy



4. X= = 0, $\Delta^{10,14}$

5. X= - α OOH, H, $\Delta^{10,14}$

6. X= - β OOH, H, $\Delta^{10,14}$

7. X= - β OH, H, $\Delta^{10,14}$

8. X= - α OH, H, $\Delta^{9,10}$

Fig. 1: 1a. Desacetyl-laurenobiolide 1. spiciformin; 2. Isospiciformin; 3. Mucrin; 4. Tamirin; 5. 1 α -hydroperoxy-1-desoxo-chrysanolide; 6. 1 β hydroperoxy-1-desoxo-chrysanolide; 7. TatrudinB; 8. Tatrudin A

These chemical constituents have previously been isolated from different species of Asteraceae but they are new for the genus *Brachanthemum*. It has to be noted that *B. gobicum* is not known as a medicinal plant, though it has the potential to become a source for isolation of biologically active compounds.

Table 3: Chemical constituents of the new essential oil endemic plants of genus *Ferula ferulaeoides* from Mongolian Gobi

Compounds (%)	Species <i>Ferula ferulaeoides</i>	
	Oil of herb	Oil of resin
α -pinene	1.62	0.28
camphene	0.20	0.12
β -pinene	1.32	0.04
myrcene	0.72	0.32
p-cymene	0.40	0.10
limonene	0.10	0.85
γ -terpinene	0.52	0.10
terpinolene	0.41	0.12
1.8-cineole	4.40	0.12
α -thujone	0.36	0.10
camphor	0.40	0.10
borneol	0.24	0.10
terpin-4-ol	0.21	0.10
α -terpineol	0.20	-
Endo-fenchylacetate	3.00	1.17
bornylacetate	3.40	1.20
α -ylangene	0.25	-
daucene	1.65	-
β -caryophyllene	0.34	0.24
α -bergamotene	0.79	-
α -guaiene	1.20	0.10
α -himachalene	1.10	0.10
β -farnesene	4.36	3.02
acoradiene	1.82	-
γ -curcumene	0.59	0.55
α -selinene	-	0.76
(E)- β -farnesene	1.10	-
β -bisabolene	1.45	1.34
γ -cadinene	0.92	0.10
(E)- β -bisabolene	0.87	0.10
δ -cadinene	0.38	0.10
α -calocorene	0.43	-
β -hydroagarofuran	1.71	0.44
5-neocedramol	0.85	-
β -agarofuran	0.48	-
(E)-nerolidol	10.06	10.20
guaicol	18.81	58.76
10-eqi- γ -eudesmol	9.92	0.60
γ -eudesmol	1.10	0.10
α -eudesmol	1.83	-
bulnesol	0.86	0.82
β -bisabolol	2.01	0.10
juniper camphor acetate	0.84	-
Monoterpene hydrocarbons	7.60	2.70
Oxygenated monoterpenoids	16.92	4.44
Sesquiterpene hydrocarbons	17.25	5.90
Oxygenated sesquiterpeneoids	53.03	70.78
Total	94.80	83.82

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