Volatile Components of the Essential Oils of Four Chinese Species in the Genus *Asarum* (Aristolochiaceae)

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Z. Naturforsch. **45c,** 32–36 (1990); received February 20/September 18, 1989

Essential Oil, Terpene, Phenol Ether, Chemosystematics

The volatile components of the essential oils of four Chinese species in the genus *Asarum* were investigated by means of GC-MS. Large amounts of elemicin, safrole, and 2-undecane together with several mono- and sesquiterpenes were identified in the essential oils. It was found that Chinese *Asarum* species is similar phytochemically to the genus *Heterotropa* in Japan.

Introduction

The genus *Asarum* of Aristolochiaceae with about 100 species has a wide distribution in Asia, Europe, and North America. The genus has its center of distribution in Eastern Asia, especially in Japan and China. According to the Engler's classification [1], all species are placed in one genus *Asarum*. In contrast, in Maekawa's [2] and Bromquist's [3] systems, the genus is divided into five genera: *Asarum, Asiasarum, Heterotropa, Geotaenium,* and *Hexastylis*. Recently, Cheng and Yang [4] reported that thirty-one *Asarum* species in China are divided into two subgenera *(Asarum, Heterotropa)* and are distributed mainly along the Yangtze River. In this work, Cheng's classification was used as genus *Asarum,* subgenera *Asarum* and *Heterotropa* for Chinese *Asarum* species. On the other hand, Maekawa's and Bromquist's systems are used for all the species distributed in Japan, Formosa, and North America.

In their phytochemical study, Yang *et al.* [5] reported the analysis of the volatile components of crude drugs (dry material) of thirty-one Chinese species in genus *Asarum*. The analytical data are very useful for pharmacology but does not use for phytochemistry because of the susceptible to isomerization of the volatile components such as terpenes.

In the course of a systematic study of the *Asarum* species, we have been investigated the volatile components of forty-three species (genus *Heterotropa*) in Japan, three species (genus *Heterotropa*) in Formosa, and two species (genus *Hexastylis*) [5] in North America. Maekawa [2] suggested that the *Heterotropa* species in Japan are originated from Szechuan or Yunnan Province in China. In order to clarify the origin and distribution of Japanese *Heterotropa* species, we examined the volatile components of the essential oils of four typical Chinese species belonging to both subgenus *Asarum (A. caudigerum, A. cardiophyllum)* and subgenus *Heterotropa (A. chingchengense, A. delavayi)* in Yunnan Province.

Experimental

Isolation and identification of the essential oils

The four *Asarum* species (*A. caudigerum* Hance, *A. chingchengense* C. Y. Cheng *et* C. S. Yang, *A. delavayi* Fr., *A. cardiophyllum* Fr. were collected from Chatung area in Yunnan Province in China in July and identified by one of the authors (Zonglian Chen). These voucher specimens are available for inspection at Herbarium of the Kunming Institute of Botany, The Academy of Sciences of China. The essential oils of the fresh leaves and roots of four *Asarum* species were obtained by steam distillation. The individual components of the essential oils were identified by means of GC-MS [6]. The data were obtained by Finnigan-4510 GC-MS Instrument using SE-54 silica capillary column (30 m × 0.25 mm) under the following conditions: column T; 80 to 200 °C at a rate of 3 °C, Ion Source T; 140 °C, Ionization Voltage; 25 and 70 eV.

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Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen
0341–0382/90/0100-0032 $ 01.30/0

Statistical analysis of the components of Asarum species

All analyses were done using NEC PC-9801 personal computer equipped with multivariate analysis program soft by Microsystem Co. Ltd., Japan. We used a cluster (dendrogram) analysis in order to examine similarity among species. The distance measure used was 1-γ (γ = Peason Correlation Coefficient) and centroid (average) clustering.

Results and Discussion

Analytical data

The analytical results of the essential oils of the four Chinese species in the genus *Asarum* examined in this work were as follows:

A. caudigerum Hance (subgenus *Asarum*)

Leaves: leaf oil 0.03% yield, myrcene (0.01%), 2,2-dimethyl hexane (0.02%), 2-ethyl-1-hexanol and *p*-cymene (0.04%), *E*-β-ocimene (0.09%), 2-nonanone (1.52%), linalool (0.05%), nonanal (0.06%), camphor (0.03%), 2-undecanone (49.26%), *p-tert*-butyl phenol (0.14%), δ-elemene (2.68%), *n*-tridecane (0.02%), α-copaene (0.04%), bourbonene (0.04%), β-elemene (0.15%), δ-selinene (0.22%), aromadendorene (0.25%), β-farnesene (0.15%), alloaromadendorene (1.22%), γ-muurolene (0.84%), β-maaliene (0.83%), γ-elemene (4.36%), 2-tridecanone (2.35%), 2,6-di-*tert*-butyl-4-methylphenol (9.05%), δ-cadinene (0.14%), α-bisabolene (0.87%), elemol (0.23%), nerolidol (0.03%), δ-cadinol (1.13%), β-bisabolol (2.75%), β-eudesmol (0.12%), myristic acid (0.13%), dibutylphthalate (0.17%), palmitic acid (0.29%), ethylpalmitate (0.04%), phytol (0.11%), unknown (20.57%).

Roots: roots 0.08% yield, α-pinene (0.02%), camphene (0.01%), sabinene (0.01%), β-pinene (0.20%), myrcene (0.09%), α-phellandrene (0.46%), *p*-cymene (0.10%), sylvestrene (0.13%), *E*-β-ocimene (0.24%), 2-nonanone (4.09%), camphor (trace), 2-decanone (0.01%), decanal (0.03%), cumic acid (0.12%), 2-undecanone (68.61%), *p*-butylphenol (0.02%), δ-elemene (0.20%), terpinyl acetate (0.03%), β-elemene (0.06%), δ-selinene (0.54%), aromadendrene (0.20%), 4-phenyl-4-methyloctane (0.10%), *E*-β-farnesene (0.05%), alloaromadendrene (0.83%), γ-muurolene (0.23%), β-maaliene (0.87%), 2-tridecanone (9.96%), 2,6-di-*tert*-butyl-4-methyl phenol (0.62%), α-bisabolene (0.36%), elemol (0.04%), nerolidol (0.20%), dodecanoic acid (0.11%), δ-cadinol (6.24%), 2-pentadecanone (0.16%), tetradecanoic acid (0.06%), 9,11-octadecadienal (0.03%), unknown (4.97%).

A. chingchengense C. Y. Cheng *et* C. S. Yang (subgenus *Heterotropa*)

Leaves: leaf oil 0.09% yield, methyl-2-hydroxyisovalerate (0.04%), α-thujene (0.01%), α-pinene (0.70%), camphene (0.65%), sabinene (0.03%), β-pinene (1.14%), myrcene (3.80%), 2-ethyl-1-hexanol (0.19%), 1,8-cineole (0.82%), *E*-β-ocimene (0.31%), terpinolene (0.01%), linalool (2.72%), 2-methyl-3-ethylheptane (0.02%), camphor (1.82%), borneol (0.45%), 4-terpineol (0.05%), naphthalene (0.04%), α-terpineol (0.04%), 2,4,6-trimethylacetophenone (0.01%), bornyl acetate (0.02%), safrole (0.26%), eugenol (0.02%), α-copaene (0.03%), bourbonene (0.11%), β-elemene (0.89%), methyleugenol (2.91%), 2,3,5-trimethoxybenzene (2.46%), β-caryophyllene (5.91%), β-gurjunene (0.54%), *Z*-β-farnesene (0.07%), acoradiene (1.40%), γ-muurolene (1.96%), β-selinene (0.08%), asaricin (46.08%), 2,6-di-*tert*-butyl-4-methylphenol (2.23%), elemicin (9.40%), nerolidol (0.24%), 2,4-dimethoxyphenyl-1-propanone (0.02%), δ-cadinol (0.01%), asarone (0.01%), patchouli alcohol (0.05%), heptadecane (0.08%), octadecane (0.05%), 6-methyloctadecane (0.09%), nonadecane (0.05%), methyl palmitate (0.05), dimethylphthalate (0.07%), palmitic acid (0.47%), eicosane (0.02%), unknown (11.57%).

Roots: root oil 0.13% yield, 2-furaldehyde (trace), methyl 2-hydroxy-3-methyl butanate (0.01%), α-thujene (0.06%), α-pinene (4.22%), camphene (3.80%), sabinene (0.06%), β-pinene (4.27%), 7-octen-4-ol and β-myrcene (0.06%), α-terpinene (0.01%), 2-ethyl-1-hexanol (0.03%), 1,8-cineole (1.48%), Δ^4-carene (0.03%), isoterpinene (0.01%), camphor (2.48%), camphene hydrate (0.03%), borneol (0.95%), 4-terpineol

(0.19%), naphthalene (0.01%), α-terpineol (0.06%), cumic acid (0.01%), 2,4,6-trimethylphenylethane (0.02%), 3,5-di-methoxytoluene (3.29%), bornyl acetate (0.06%), α-copaene (0.01%), β-elemene (0.05%), 4-phenyl-4-methyloctane (5.33%), 2,3,5-trimethoxytoluene (3.95%), β-gurjunene (0.37%), α-guaiene (0.07%), acoradiene (0.43%), γ-elemene (0.24%), myristicin (0.35%), δ-guaiene (0.10%), 2,6-di-*tert*-butyl-4-methylphenol (1.36%), elemol (0.02%), elemicin (65.44%), euasarone (0.10%), 6-methoxyelemicin (0.06%), 6-methoxyeugenol (0.13%), 2,3-dimethoxyeugenol (0.04%), kakuol (0.08%), isoelemicin (0.04%), patchouli alcohol (0.09%), hexachlorobenzene (0.01%), dibutylphthalate (0.02%), palmitic acid (0.12%), unknown (0.45%).

A. delavayi Fr. (subgenus *Heterotropa*)

Leaves: leaf oil 0.12%, α-thujene (0.01%), α-pinene (0.45%), camphene (0.23%), sabinene (0.16%), β-pinene (0.46%), 7-octen-4-ol (0.12%), α-phellandrene (0.15%), Δ^3-carene (0.46%), *p*-cymene (0.15%), sylvestrene (1.66%), 1,8-cineole (0.58%), ocimene (0.08%), Δ^4-carene (0.05%), terpinolene (0.06%), linalool (0.34%), camphor (0.47%), borneol (0.17%), 4-terpineol (0.30%), α-terpineol (0.20%), safrole (87.08%), eugenol (0.20%), α-copaene (0.03%), β-elemene (0.08%), 2,3,5-trimethoxytoluene (0.85%), 2,4,5-trimethoxytoluene (0.27%), β-caryophyllene (0.52%), *E*-β-farnesene (0.27%), humulene (0.03%), γ-muurolene (0.07%), 2,6-di-*tert*-butyl-4-methylphenol (1.87%), δ-cadinene (0.08%), elemicin (0.02%), nerolidol (0.17%), palustrol (0.32%), 4-allyl-2,6-dimethoxyphenol (0.28%), octadecane (0.02%), di-octylphthalate (0.07%), palmitic acid (0.24%), unknown (1.43%).

Roots: root oil 1.08%, α-thujene (0.02%), α-pinene (1.54%), camphene (1.08%), sabinene (0.35%), β-pinene (2.42%), α-phellandrene (0.17%), α-terpinene (0.06%), *p*-cymene (0.06%), limonene and ocimene (0.35%), 1,8-cineole (3.30%), Δ^4-carene (0.28%), terpinolene (0.08%), linalool (0.03%), camphor (1.87%), borneol (3.11%), 1,4-cineole (0.02%), 4-terpinenol (0.16%), α-terpineol (0.16%), 3,5-dimethoxytoluene (42.60%), safrole (5.01%), eugenol (0.17%), α-cubebene (0.03%), α-cedrene (0.02%), β-elemene (0.16%), δ-selinene (9.22%), 2,3,5-trimethoxytoluene (12.34%), 2,4,5-trimethoxytoluene (2.52%), aromadendrene (0.44%), α-guaiene (0.17%), α-patchoulene (0.14%), β-selinene (0.27%), δ-guaiene (0.27%), 2,6-di-*tert*-butyl-4-methylphenol (0.53%), γ-cadinene (0.09%), γ-elemene (0.21%), nerolidol (1.36%), palustrol (0.49%), 6-methoxyeugenol (0.08%), viridiflorol (0.07%), patchouli alcohol (1.08%), palmitic acid (0.08%), methyl-11,14-eicosadienoate (0.09%), unknown (7.50%).

A. cardiophyllum (subgenus *Asarum*)

Leaves: leaf oil 0.17% yield, α-pinene (0.01%), camphene (trace), β-pinene (0.10%), myrcene (0.14%), α-phellandrene (0.05%), 2-ethyl-1-hexanol (0.12%), linalool (0.62%), camphor (0.42%), borneol (0.04%), 4-terpineol (0.05%), naphthalene (0.07%), 3,5-dimethoxytoluene (0.49%), hexyl acetate (0.04%), safrole (0.08%), *n*-tridecane (0.12%), δ-elemene (0.20%), β-elemene (5.71%), methyleugenol (0.43%), 3,4,5-trimethoxytoluene (0.08%), β-caryophyllene (0.15%), aromadendrene (0.06%), α-guaiene (0.17%), *E*-β-farnesene (0.16%), α-humulene (0.17%), γ-muurolene (0.31%), β-selinene (0.44%), *n*-pentadecane (5.51%), γ-elemene (6.25%), 2,6-di-*tert*-butyl-4-methylphenol (8.42%), δ-cadinene (0.29%), α-bisabolene (2.67%), elemicin (52.88%), δ-cadinol (0.14%), euasarone (0.81%), heptadecane (0.30%), 1-heptadecanol (0.97%), myristic acid (0.23%), pentadecanoic acid (0.15%), dimethylphthalate (1.24%), palmitic acid (0.79%), unknown (9.12%).

Roots: root oil 0.21%, α-pinene (0.01%), camphene (0.01%), β-pinene (0.04%), myrcene (0.12%), α-phellandrene (0.03%), Δ^3-carene (0.30%), *p*-cymene (0.11%), sylvestrene (0.07%), *Z*-β-ocimene (0.01%), terpinolene (0.04%), linalool (0.15%), 6-methyl-3,5-heptadien-2-one (0.01%), 1-cyclohexylidene-2-propanone (0.02%), camphor (0.01%), *p*-cymene-alpha-ol (0.01%), α-terpineol (0.01%), bornyl acetate (0.06%), eucarvone (0.02%), β-elemene (0.04%), methyleugenol (0.66%), β-farnesene (0.02%), β-selinene (0.03%), γ-elemene (0.25%), 2,6-di-*tert*-butyl-4-methylphenol (0.64%), α-bisabolene (0.33%), elemicin (92.37%), 3,4,5-trimethoxybenzaldehyde

(0.17%), *cis*-asarone (0.09%), isoelemicin (3.13%), *trans*-asarone (0.11%), unknown (1.13%).

Chemosystematic aspects of four Chinese species in genus Asarum

The essential oils of *A. caudigerum* in the subgenus *Asarum* contained a characteristic component, 2-undecanone in the leaves (49.20%) and roots (68.61%) together with considerable amounts of mono- and sesquiterpenes but no phenylpropanes. Phytochemically, the presence of the ketone in the essential oils of *Asarum* species is significant. On the other hand, the essential oils of *A. cardiophyllum* in the same subgenus *Asarum* contained a high quantity of elemicin in the leaves (52.88%) and roots (92.37%). The components of this species are very similar to those of genus *Heterotropa* in Japan. The leaf oils of *A. chingchengense* in the subgenus *Heterotropa* contained asaricin (46.08%), while the root oils contained elemicin (65.44%) as a main components. The essential oils of the fresh leaves of *A. delavayi* contained a high level of safrole (87.08%) and the roots oil contained a large amount of 3,5-dimethoxytoluene (42.60%).

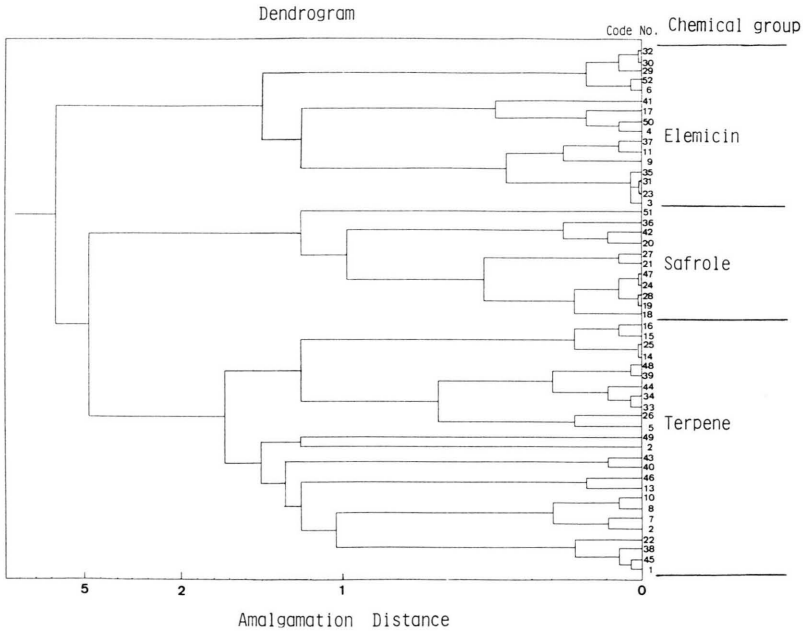

Fig. 1. Dendrogram constructed from chemical parameters of the 52 species in the genus *Asarum* by the use of cluster analysis. Code number: (1) *Heterotropa tamaensis* F. Maekawa, (2) *H. Muramatui* F. Maekawa, (3) *H. savatieri* Franch, (4) *H. koyana* var. *nipponica* (F. Maekawa) Kitam., (5) *H. curvistigma* F. Maekawa, (6) *H. kurosawae* F. Maekawa, (7) *H. megacalyx* F. Maekawa, (8) *H. yoshikawae* F. Maekawa, (9) *H. nipponica* var. *brachypodion* F. Maekawa, (10) *H. nipponica* var. *rigescens* F. Maekawa, (11) *H. takaoi* F. Maekawa, (12) *H. coststus* F. Maekawa, (13) *H. nankaiensis* F. Maekawa, (14) *H. sakawana* (Makino) F. Maekawa, (15) *H. stelleta* F. Maekawa, (16) *H. aspera* F. Maekawa, (17) *H. hexaloba* F. Maekawa, (18) *H. nomurana* F. Maekawa, (19) *H. asaroides* Morren et Decaisne, (20) *H. kuranarii* F. Maekawa, (21) *H. kiusiana* F. Maekawa, (22) *H. unzen* F. Maekawa, (23) *H. controversa* F. Maekawa, (24) *H. subglobosa* F. Maekawa, (25) *H. minamitaniana* F. Maekawa, (26) *H. perfecta* F. Maekawa, (27) *H. satsumensis* F. Maekawa, (28) *H. trigyna* (F. Maekawa) Araki, (29) *H. kumageana* var. *satakeana* F. Maekawa, (30) *H. kumageana* (Masamune) F. Maekawa, (31) *H. yakusimensis* Masamune, (32) *H. tokarensis* Hatusima, (33) *H. gusuk* F. Maekawa, (34) *H. celsa* F. Maekawa, (35) *H. lutchuensis* (T. Ito) Honda, (36) *H. fudsinoi* (T. Ito) F. Maekawa, (37) *H. trinacriformis* F. Maekawa, (38) *H. hatusima* F. Maekawa, (39) *H. similis* F. Maekawa, (40) *H. okinawensis* (Hatusima) F. Maekawa, (41) *H. dissita* F. Maekawa, (42) *H. gelasina* (F. Maek.) F. Maekawa, (43) *H. yaeyamaensis* (Hatusima) F. Maekawa, (44) *H. hayatana* F. Maekawa, (45) *Heterotropa* sp. (Daiton kanaoi), (46) *H. macranta* F. Maekawa, (47) *Hexastylis arifolia* (Machx.) Small, (48) *Hexastylis minus* (L.) Small, (49) *Asarum caudigerum* Hance, (50) *A. chingchengense* C. Y. Cheng *et* C. S. Yang, (51) *A. delavayi* Fr., (52) *A. cardiophyllum* Fr.

The dendrogram of the results of cluster analysis of four Chinese species together with 48 species (distributed in Japan, Formosa, North America) based on the volatile components (phenylpropanes, terpenes, orcinol derivatives) of the whole plants is shown in Fig. 1. The cluster membership of the species is indicated by the code number 1–52, in which Chinese species are code No. 49–52. Based on the dendrogram, three chemical groups (safrole, elemicin, and terpene groups) in genus *Asarum* could be distinguished.

A. caudigerum (code No. 49) in the subgenus *Asarum* belongs to the terpene group, while *A. caudigerellum* (code No. 52) in the same subgenus belongs to the elemicin group. *A. chingchengense* in the subgenus *Heterotropa* belongs to elemicin group and *A. delavayi* (code No. 51) in the same subgenus belongs to the safrole group.

The composition of genus *Asarum* (one species in Japan) and genus *Asiasarum* (four species in Japan) has been examined by Endo [7]. The species in the genus *Asarum* in Japan contained a large amount of sesquiterpenes together with small quantities of monoterpenes but no phenylpropanes, while the four species in the genus *Asiasarum* contained both terpenes and phenyl ethers. The genus *Heterotropa* in Japan have been investigated by our group [8], and most of the species in the genus *Heterotropa* contained phenol ethers (safrole, elemicin, 1-allyl-2,3,4,5-tetramethoxybenzene) and terpenes as main components.

A. europaeum L. (in Europe) [9] contained phenol ethers (*trans*-isoasarone, isomethyleugenol, *trans*-isoeugenol) and terpenes (borneol, bornyl acetate, eudesmol) as main components. The American *Hexastylis* [10] contained phenol ethers (safrole, methyleugenol, elemicin) and terpenes in the essential oils.

Considering these results from view-point of chemosystematics, it was found that the components of the three Chinese species (*A. caudigerellum, A. delavayi, A. chingchengense*) are closely similar to those of the species of genus *Heterotropa* in Japan and *Hexastylis* in North America, while the components of *A. cardiophyllum* are similar to those of genus *Asarum* in Japan phytochemically.

Acknowledgements

The authors wish to thank Professor Jun Zhou and Dr. Chong Ren Yang (Kunming Institute of Botany, The Academy of Sciences of China) for their encouragement throughout this work.

[1] A. Engler, Syllabus der Pflanzenfamilien **11,** 152 (1964).
[2] F. Maekawa, J. Japan Botany **9,** 39, 96, 174, 241, 281, 364, 505 (1933).
[3] L. Bromquist, Brittonia **8,** 195 (1957).
[4] C. Cheng and C. Yang, J. Arnold Arboretum **64,** 565 (1983).
[5] C. Yang, J. Zhang, J. Pang, Z. Xu, Q. Zhu, and G. Wang, Zhongyao Tongbao (Bull. Chinese Mat. Med.) **1984,** 9, 27, 175, and **1986,** 11, 46, 423.
[6] S. R. Heller and G. W. A. Milne, EPA/NIH "Mass Spectral Data Base", U.S. Government Printing Office, **Vol. 1–4** (1980).
[7] J. Endo, T. Ogino, and M. Nagasawa, Yakugaku Zassi. **92,** 874 (1972); J. Endo and M. Nagasawa, ibid. **94,** 1574 (1974); J. Endo, ibid. **95,** 1321 (1975); J. Endo, T. Nakamura, M. Nagasawa, ibid. **51,** 209 (1976); J. Endo, ibid. **97,** 393 (1977); J. Endo and T. Nagasawa, ibid. **98,** 789 (1978).
[8] B. M. Lawrence, B. D. Mookherjee, and B. J. Willis, Flavors and Fragrances, pp. 259–282, Elsevier Science Publishing B. V., Amsterdam 1988.
[9] W. E. Biering, I. Bungert-Hansing, and H. Jork, Planta Med. **29,** 133 (1976).
[10] N. Hayashi, K. Maeshima, and H. Komae, Phytochemistry **22,** 299 (1983).