Putative late Pleistocene hybrids inferred from volatile leaf oils (terpenoids) of *Cupressus chengiana*

Robert P. Adams
Baylor University, Biology Department, Utah Lab, Baylor University, Waco, TX 76798, USA
robert_adams@baylor.edu

Jia-Liang Li and **Kang-Shan Mao**
Key Lab of Bio-resources and Eco-environment, Ministry of Education, College of Life Sciences, Sichuan University, Chengdu, Sichuan 610064, China, maokangshan@scu.edu.cn

ABSTRACT

An investigation of variation in essential leaf oils of *Cupressus chengiana* from three populations (BLJ, Gansu; DDH, Sichuan, MJR, Sichuan) found the oils were high to moderate amounts of sabinene, α-pinene, myrcene, limonene, β-phellandrene, γ-terpinene, umbellulone, terpinen-4-ol, δ-cadinene, germacrene-D, elemol, hedycaryol, iso-abienol, and trans-totarol. A Minimum Spanning Network based on 15 major terpenoids revealed the 34 oils grouped by population, except 5 trees from DDH had oils more like BLJ plants. PCO ordination showed the 5 unusual DDH oils grouped in a position suggesting they are hybrids or of hybrid origin. The ordination of one plant suggested it may be a backcross to BLJ plants. DNA sequencing has inferred that DDH and BLJ ancestors hybridized during the Quaternary (Li et al. 2020), but the presence of chemical intermediate oils in DDH, seems to imply that more recently (late Pleistocene), a second hybridization event occurred between DDH and BLJ. Correlation among the 15 major compounds revealed high correlation between structurally similar compounds. The potential use of the presence of several chemical-types to analyze biochemical pathways is discussed. *Published on-line www.phytologia.org Phytologia 1022(2): 41-54 (June 24, 2020). ISSN 030319430.*

KEY WORDS: *Cupressus chengiana*, leaf terpenoids, essential oils, composition variation, sabinene, α-pinene, umbellulone, elemol, eudesmols, trans-totarol.

Cupressus chengiana S. Y. Hu, the Minjiang cypress, grows in the eastern Qinghai-Tibet Plateau (QTP), mostly in arid valleys at the headwaters of three rivers: Sichuan: Minjiang and Daduhe rivers, and Gansu: Bailongjiang river (Fig. 1), at 800 to 2900 m (Xu et al. 2017; Li et al. 2020). The Minjiang cypress has experienced a large decline in population sizes due to logging and grazing (Hao et al. 2006) and, as such, has been listed as 'Second-class Endangered Plant' in the *Red Book of China: Rare and Endangered Plants* (Fu, 1992). Xu et al. (2017) found evidence of reduced gene flow between the Gansu and Sichuan populations.

Li et al. (2020) studied *C. chengiana* sampled from DDH, MLR populations in Sichuan and BLJ populations in Gansu (Fig. 1). Using High-throughput Sequencing (HTS), they utilized 31,527 nuclear SNPs for phylogenetic analysis of the three groups. A ML tree based on these nuclear data (Fig. 2) shows that the three taxa (or ESU, Evolutionary Significant Units) are in three highly supported, distinct clades: DDH, MRJ and BLJ.

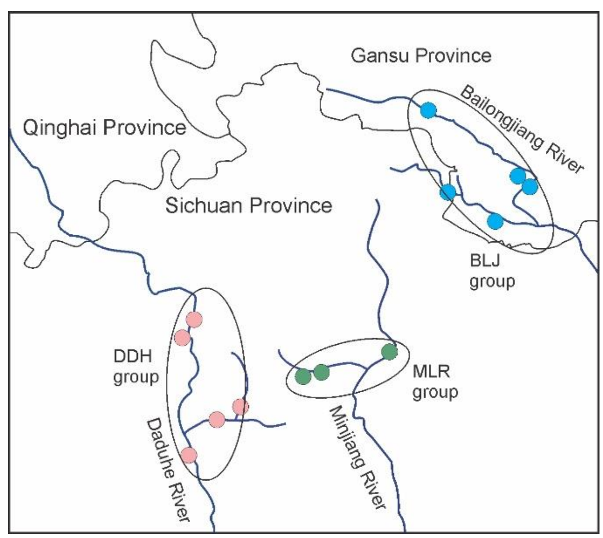

Figure. 1. Distribution of *C. chengiana* populations sampled (adapted from Li et al. 2020).

MJR group, Minjiang River, Sichuan grouped with the BLJ group, Gansu, but appeared intermediate in a PCA ordination (Li et al. 2020). In fact, Li et al. (2020) also investigated cp (chloroplast) ML tree and found that DDH and MJR apparently share the same cp haplotype lineage, as the DDH and MJR samples were all intermixed in a distinct clade in the ML tree, and grouped in highly supported clades as ((DDH, MJR), (BLJ). This is excellent evidence of chloroplast capture (see Adams, Schwarzbach and Tashev, 2016; Adams 2016; Farhat et al. 2019; Hojjati et al. 2019; Adams et al. 2017). Thus, *C. chengiana*, MJR group, on the Minjiang River, appears to be of hybrid origin between male DDH and female BLJ in the Quaternary when the groups descended to lower, warmer, dryer, elevations to produce areas of sympatry (Li et. al. 2020).

The DDH, MJR and BLJ ESUs (taxa) are, morphologically, difficult to distinguish. With the collection of extra foliage in the Xu et al (2017) field study, this presented us with an unusual opportunity to examine the volatile leaf oil of *C. chengiana* from the three DDH, MJR and BLJ taxa.

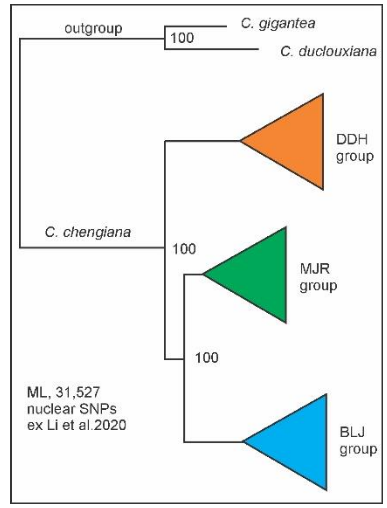

Fig. 2. ML tree showing the grouping of MJR and BLJ. Based on data in Li et al. 2020.

The volatile leaf oil of *C. chengiana* has not been extensively analyzed. The most detailed report on the composition (Cool et al. 1998) was from oil obtained from a natural population (10 samples) at Wu Du, Gansu (Kansu), 33˚ 34' N, 104˚ 55' E, 1500m. This corresponds to the BLJ population group, site Wudu (Table 1, Xu et al. 2017). Cool et al. (1988) reported the oil was dominated by sabinene (24.9%), elemol/hedycaryol (14.5%), trans-totarol (11.7%), with moderate amounts of α-pinene (5.8%), β-pinene (2.8%), limonene (2,2%), germacrene-D (2.5%), iso-abienol (3.1%), and sempervirol (2.4%).

Li et al. (2005) analyzed the leaf essential oils from three natural populations on the Minjiang and Daduhe rivers and one man-made forest in Wenchuan. The oil from the artificial forest was quite different from the oils the three natural populations. The concentrations of the larger components of the oil from the three natural populations were similar. Analysis of the leaf oil of *C. chengiana* cultivated in France (Pierre-Leandri et al. 2003) reported that α-pinene (17.6%) and sabinene (32.1%) were the major components, with moderate amounts of myrcene (3.6), α-terpinene (2.5), limonene (+β-phellandrene?) (5.3), terpinolene (2.4), terpinen-4-ol (11.3) and elemol (2.9%). Unfortunately, the origin of their *C. chengiana* was only given as 'China', so we cannot know if he analyzed DDH, MRJ or BLJ plant(s).

The purpose of this paper is to present a detailed analysis of the oil compositions DDH, MRJ or BLJ plants as collected and examined by Xu et al. 2017 and Li et al. 2020.

MATERIALS AND METHODS

Plant collection of *C. chengiana* by locations:
Population DDH *Lab acc. Robert P. Adams 15732-15743*(12): 31˚ 01' 44.93" N 102° 15' 0.93" E., 2252.8 - 2711.7 m, Aug 2019, Sichuan, China Coll. Kangshan Mao. ns. LXT-05;

Population MJR *Lab acc, Robert P. Adams 15744-15753*(10): 31° 38' 23.52" N 103° 48' 20.97" E., 1742.68- 2073.3 m, Aug 2019, Sichuan, China, Coll. Kangshan Mao, ns. LXT-16;

Population BLJ: *Lab acc. Robert P. Adams 15754-15765(12)*: 33° 15' 11.82" N 104° 59' 01.44" E., 1742.68- 2073.3 m, Aug 2019, Gansu China
Coll. Kangshan Mao, ns. ZR-20;

Isolation of Oils - Fresh leaves (200 g) were steam distilled for 2 h using a circulatory Clevenger-type apparatus (Adams, 1991). The oil samples were concentrated (ether trap removed) with nitrogen and the samples stored at -20ºC until analyzed. The extracted leaves were oven dried (100ºC, 48 h) for determination of oil yields.

Volatile oil Analyses - Oils from 10-12 trees of each of the taxa were analyzed and average values are reported. The oils were analyzed on a HP5971 MSD mass spectrometer, scan time 1/ sec., directly coupled to a HP 5890 gas chromatograph, using a J & W DB-5, 0.26 mm x 30 m, 0.25 micron coating thickness, fused silica capillary column (see Adams 2006 for operating details). Identifications were made by library searches of the Adams volatile oil library (www.juniperus.org, Adams, 2006), using the HP Chemstation library search routines, coupled with retention time data of authentic reference compounds. Quantitation was by FID on an HP 5890 gas chromatograph using a J & W DB-5, 0.26 mm x 30 m, 0.25 micron coating thickness, fused silica capillary column using the HP Chemstation software.

Data Analysis - Terpenoids (as per cent total oil) were coded and compared among the species by the Gower metric (1971). Similarities between oils were computed as formulated by Adams (1975). PCO (Principal Coordinate analysis) was performed by factoring the similarity matrix using the formulation of Gower (1966) and Veldman (1967). PCA (Principal Component Analysis) done on the raw % concentration data for 15 terpenoids for each of the 34 individuals using a Fortran program (RPA) based on the formulation in Veldman (1967).

RESULTS

The composition of the leaf essential oils of *C. chengiana* for populations DDH, MJR, and BLJ, were found to be quite variable with chemotypes (cpds. being absent/present among samples). To explore the variation in oil composition, 15 of the terpenoids of largest concentration were coded and analyzed by a minimum spanning network (MSN) and this revealed the three taxa (ESUs), BLJ, DDH and MJR are mostly distinct (Fig. 3). BLJ oils formed a very tight cluster for samples B2, B4-B6, B8-B10. However, three oils, B1, B3, and B7, were quite different from the typical BLJ oils (Fig. 3). Notice that B1 and B3 are not very similar to any of the oils (Fig. 3).

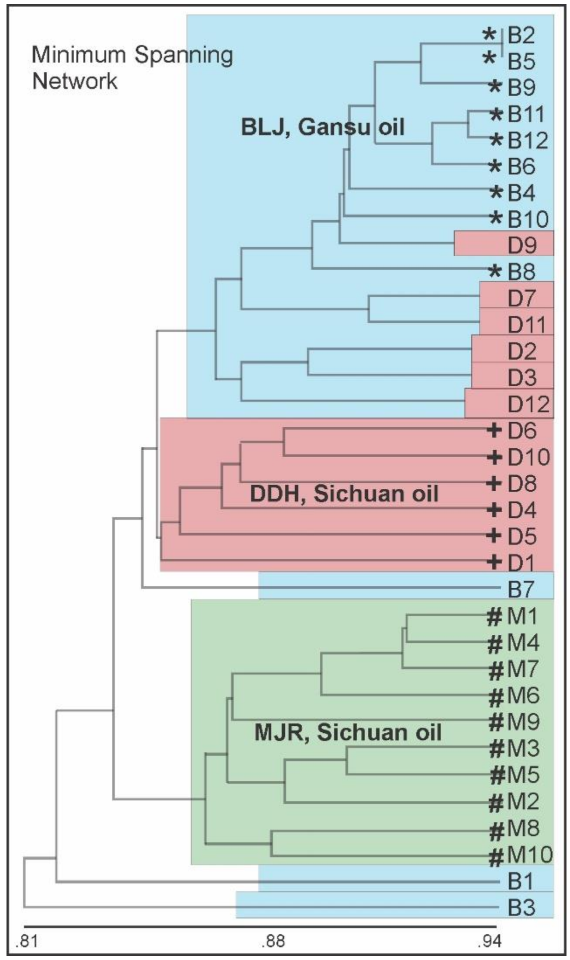

Figure 3. MSN (Minimum Spanning Network) based on 15 cpds. Individuals with *, +, # were used in the Avg. oils for DDH, MJR and BLJ.

Six of the DDH oils (D9, D7, D11, D2, D3, and D12 were most similar to the BLJ oils (Fig. 3). This might indicate that these plants are of hybrid origin as the terpenoids are inherited as intermediate concentration, dominant/ recessive and/ or transgressive (larger or smaller than the compound in either parent) (*Cryptomeria*, Adams and Tsumura 2012; *Pseudotsuga*, Adams and Stoehr 2013).

Table 1 reveals that only a few compounds distinguish between all three MRJ, DDH and BLJ oils (Table 1). The most predictive compound is sabinene: MRJ, low: 6.0%; DDH, medium: 11.3%, BLJ, high:

24.5%). The MJR oil is lower in sabinene and terpen-4-ol. DDH and MJR (ex Sichuan) are high in α-pinene and umbellulone and low in elemol/hedycaryol, α- and β-eudesmol, and α-cadinol. DDH and BLJ are high in sabinene, terpinen-4-ol, and low in cis-murrola-4(14),5-diene and epi-zonarene. Finally, MJR and BLJ are low in α-cadinol.

Table 1 also includes information from Cool et al. (1998). Generally, the three populations oils are very similar. Only one compound (linaly acetate) is absent in DDH and MJR, and a trace in BLJ. However, the absence of trace components is equivocal, as an increased injection of oil can generate sufficient ions in mass spectroscopy to detect that the compound as 'present'.

BLJ and Cool (both ex Gansu) are both high in sabinene and elemol/hedycaryol and lower in α-pinene, umbellulone, cis-murrola-4(14),5-diene, and epi-zonarene. In general, the Gansu oils are very similar (BLJ and Cool, Table 1). Three unknown diterpenoid compounds were encountered in the oils of DDH, MJR, and BLJ, all with a molecular weight of 316. Interestingly, 2 of these diterpenoids (KI 2341 and 2364) were also reported as unknowns by Cool et al. (1998). Searches of NIST MS database revealed no similar compounds. Isolation and NMR will be needed to identify these compounds.

A detailed analyses (Table 1) of volatile leaf oil compositions with the 2 (D7, D9, D11 not shown due to space) of the 6 DDH oils (D9, D7, D11, D2, D3, and D12), reveal that these oils are similar to BLJ Avg., in several compounds: α-thujene (1.1 - 1.3%), α-pinene (4.5 - 6.4), sabinene (28.8 - 35.7), α-terpinene (1.8 - 1.3), β-phellandrene (1.4 - 1.7%), γ-terpinene (2.3 - 2.9), cis-sabinene hydrate (0.8 - 1.2), terpinolene (1.3 - 1.6), cis-p-menth-2-en-1-ol (0.4 - 0.6), camphene hydrate (t, trace in all 3), terpinen-4-ol (5.1 - 6.6), trans-piperitol (0.2 - 0.3), bornyl acetate (t - 0.2), α-cadinol (0.4 - 1.7), abietatriene (0.2 - 0.6), iso-abienol (1.6 - 3.1) and cis-totarol, methyl ether (t - 0.3). So, it is easy to see why D7 and D9 (and D11, D2, D3, D12) cluster with BLJ.

The oils of the unusual oils of B3 and B7 are included in Table 1 (B1 oil is also unusual but not included due to space). B3 oil is very low in sabinene (only 1%) and high (14.1%) in elemol/hedycaryol (combined as they elute together and have the same MS pattern); β-eudesmol (9.0%), and α-eudesmol (7.8%). B3 is especially high in trans-totarol (16.8%). B7 oil is similar to B3, but both are very different from typical BLJ oil (Table 3).

To better visualize the relationships among the individuals, PCO was run using the 15 terpenoid set to construct a similarity matrix. Factoring the similarity matrix resulted in 7 eigenroots larger than the average matrix diagonal value. The eigenroots asymptoted after 6 roots and these accounted for only 66.84% of the variance among the 34 individuals. The presence of chemotypes among the plant oils likely creates mini-groupings that impede the extraction of variance with fewer eigenroots. The first three eigenroots accounted for 53.66% of the variance and were used for 3D PCO ordination (Fig. 4).

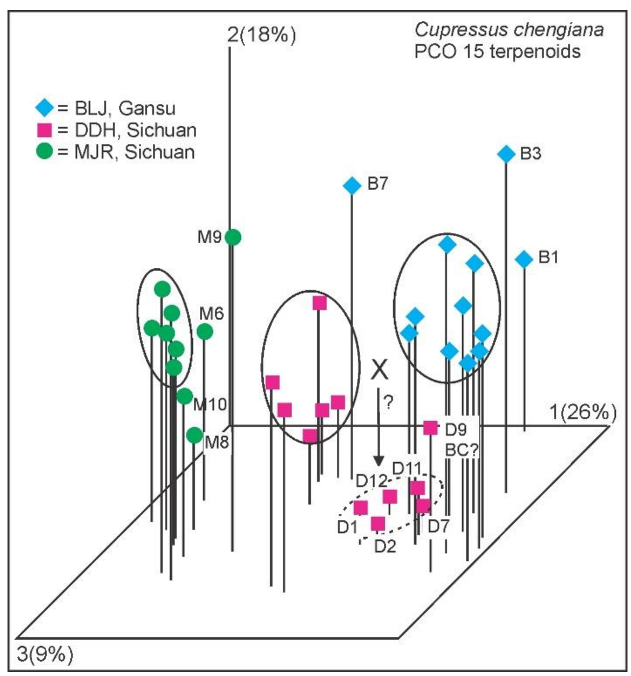

Figure 4. PCO ordination. The solid-line ellipses are the oils used to construct the averages for BLJ, DDH, and MRJ in Table 1.

The PCO ordination distinguishes the three groups (DDH, MJR, BLJ) shown by MSN (Fig. 3). MJR appears split with 4 (M6, M8, M9, M10) grouping somewhat with DDH. Oils within the BLJ solid-line ellipse are those with an * in Figure 3, and were used for the average oil in Table 1. DDH is clearly divided into the 'typical' group (+ sign in MSN, Fig. 3) and the 'hybrid' group (dashed-line ellipse) near the base of the BLJ group. Notice that the 'typical' DDH, 'typical' BLJ and the DDH 'hybrids' (dashed-line ellipse) form a 'V' or 'U'. The 'V' shape with the parents at the upper corners and the hybrids at the base of the V has been shown to be characteristic of both artificially obtained hybrids in fish and natural hybrids in *Juniperus* (Adams 1982). It has also been verified in artificial hybrids in *Cryptomeria* (Adams and Tsumura 2012) and *Pseudotsuga* (Adams and Stoehr 2013). The 'hybrids' thus appear to be from DDH x BLJ (Fig. 4). Notice that D9 is intermediate between the 'hybrids' and BLJ, and might be a backcross. The hybrid origin of MJR in Quaternary when the taxa were forced southeast of their present range into a refugium that was warmer and drier (Li et al. 2020) seems plausible. However, the, presumedly, more recent crosses of DDH x BLJ (Fig. 4), favor a second migration of DDH and BLJ in order for the taxa to be in breeding proximity. This latter hybridization event could have been recent, during the last glacial advance and retreat (ca. 12-14,000 ybp, the Late Deglaciation) (Cheng et al., 2018) with range expansion into the DDH and BLJ present ranges. One should note that it is possible that the divergent oils in the 'hybrids' may be nothing more than convergence by random drift, leading to oil profiles similar to BLJ. Additional research is needed to clarify the situation.

Correlation among terpenoids:

PCA (Principal Component Analysis) was performed to examine the correlation between the 15 major compounds (Table 2). Eigenroots from the correlation matrix asymptoted after 5 eigenroots and these accounted for 88.53% of the variance among the 15 terpenoids. The first 3 principal components accounted for 37.6, 28.4 and 13.6% of the variance among the 15 terpenoids. Ordination (Fig. 5) shows the terpenes (C10 hydrocarbons) are from two pathways: sabinene- γ-terpinene-terpinen-4-ol; and α-pinene-terpinolene-myrcene. The terpene alcohol, terpinen-4-ol, groups with the C10-HC (Fig. 5). Umbellulone (UMBO, C10-ketone) is loosely associated with the APNN-TRPN-MYRC group.

Two sesquiterpenes, δ- and γ-cadinene, are highly correlated and also correlated with germacrene D-4-ol, a sesquiterpene alcohol. The other two sesquiterpene alcohols (elemol, β-eudesmol) are highly correlated but quite separated from germacrene D-4-ol (Fig. 5). No significant amounts of diterpene hydrocarbons were present, but oxygenated diterpenes were present in the oils. Two structurally related diterpenes, trans-totarol and trans-totarol, methyl ether, are highly correlated (0.72) and group together. Another diterpene alcohol, iso-abienol, groups loosely with trans-totarol and trans-totarol, methyl ether (Fig. 5).

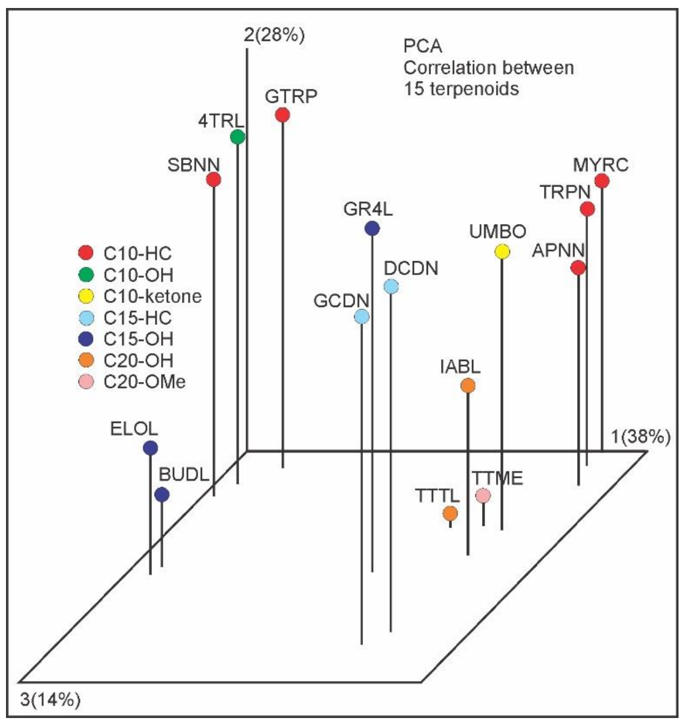

Figure 5. PCA ordination of 15 terpenoids.

Examining the populations with the 15 terpenoids, arranged in correlated groups (Table 3), clearly shows the 6 'hybrid' oils are high in sabinene as is common in the BLJ population. This is more clearly seen in Table 4, where plant oils are sorted by sabinene. Notice the highest (gold highlight) concentrations of sabinene are in 2 DDH 'hybrids' (D8, 35.7%; D11 33.2%), followed closely by 3 BLJ plants, then 4 more DDH 'hybrids' (Table 4). B3, an unusual BLJ plant, has very low sabinene. NextGen analyses comparing B3 (and also M9) exomes with D9, D11, B9, D2, B5 might prove useful in discovering differences in sabinene synthetase genes.

There are 2 chemotypes of elemol: very high and trace amounts (Table 5). NextGen analyses comparing B1 (another very unusual oil type) exome with D1, D12, D2, D3, D5, (as well as M2, M3, M5) exomes should be useful in examining differences in elemol synthetase genes.

Umbellulone is an unusual terpene ketone that is common in *Cupressus* (Cool et al. 1998). Although it is not extremely in high concentration (8.8%, D8), it is very frequently only a trace (0.05% or less) in 9 plant oils (Table 6). Again, NextGen analyses comparing the D8 exome with the exomes of D9, D11, etc., Table 6) could uncover differences in umbellulone synthetase gene(s).

Finally, germacrene D-4-ol also shows an interesting pattern (Table 7) in that the highest concentration is in one of the 'hybrids', D12 (5.8%) and the lowest concentration is in another 'hybrid' D9 (0.02%). Contrasting their exomes should prove very informative. It is significant that for the aforementioned chemotypes (sabinene, elemol, umbellulone, germacrene D-4-ol), the largest concentration was found in either D8, D9, D12 or B1. The 'hybrids' and atypical (B1) plants express transgressive variation that is a very common feature of the oils of hybrid conifers (*Cryptomeria*, Adams and Tsumura 2012; *Pseudotsuga*, Adams and Stoehr 2013).

In summary, the unusual chemical variation between and especially within BLJ and DDH populations make these resources a valuable biological resource that should be protected.

ACKNOWLEDGEMNTS

This research supported (KM) by National Natural Science Foundation of China (grants 31622015), Sichuan Provincial Department of China (grant 2015JQ0018) and Sichuan University. Additional support is acknowledged from Baylor University (project 0324512 to RPA).

LITERATURE CITED

Adams, R. P. 1975. Statistical character weighting and similarity stability. Brittonia 27:305-316.

Adams, R. P. 1982. A comparison of multivariate methods for the detection of hybridization. Taxon 31:646-661.

Adams, R. P. 1991. Cedar wood oil - analysis and properties. In Modern Methods of Plant Analysis: Oils and Waxes. H. F. Linskins and J. F. Jackson, Eds., pp. 159 - 173, Springer-Verlag, Berlin, Germany.

Adams, R. P. 2006. Identification of Essential Oils Components by Gas Chromatography/ Mass Spectrometry, 4th Ed. Allured Publ. Corp., Carol Stream, IL. 4.1, ed, 2017 pdf available at www.juniperus.org

Adams, R. P. 2016. Two new cases of chloroplast capture in incongruent topologies in the *Juniperus excelsa* complex: *J. excelsa* var. *turcomanica* comb. nov. and *J. excelsa* var. *seravschanica* comb. nov. Phytologia 98: 219-231.

Adams, R. P. and M. Stoehr. 2013. Multivariate detection of hybridization using conifer terpenes II: Analyses of terpene inheritance patterns in *Pseudotsuga menziesii* F_1 hybrids. Phytologia 95(1): 42-57.

Adams, R. P. and Y. Tsumura. 2012. Multivariate detection of hybridization using conifer terpenes I: Analysis of terpene inheritance patterns in *Cryptomeria japonica* F_1 hybrids. Phytologia 94(2): 253-275.

Adams, R. P., A. E. Schwarzbach and A. N. Tashev. 2016. Chloroplast capture by a new variety, *Juniperus sabina* var. *balkanensis* R. P. Adams and A. N. Tashev, from the Balkan peninsula: A putative stabilized relictual hybrid between *J. sabina* and ancestral *J. thurifera.* Phytologia 98(2): 100-111.

Adams, R. P., M. Socorro Gonzalez-Elizondo, Martha Gonzalez-Elizondo, David Ramirez Noy and Andrea E. Schwarzbach. 2017. DNA sequencing and taxonomy of unusual serrate *Juniperus* from Mexico: Chloroplast capture and incomplete lineage sorting in *J. coahuilensis* and allied taxa. Phytologia 99: 62-73.

Cheng, Z., C. Weng, J. Gao, L. Dai, and Z. Zhou. 2018. Vegetation responses to late Quaternary climate change in a biodiversity hotspot, the Three Parallel Rivers region in southwestern China. Palaeogeogr. Palaeoclimatol. Palaeoecol. 491: 10–20.

Cool, L. G., Z-L. Hu and E. Zavarin. 1998. Foliage terpenoids of Chinese Cupressus species. Biochem. Syst. Ecol. 26: 899-913.

Farhat, P., S. Siljak-Yakovlev, **R. P. Adams**, T. Robert and M. B. Dagher-Kharrat. 2019. Genome size variation and polyploidy in the geographical range of *Juniperus sabina* L. (Cupressaceae). Botany Letters DOI: 10.1080/23818107.2-19.1613262

Fu, L-K. 1992. Red book of China: rare and endangered plants. Science Press, Beijing.

Hao, B-Q., W. Li, L-C. Mu, Y. Li, Z. Rui, M-X. Tang and W-K. Bao. 2006. A study of conservation genetics in *Cupressus chengiana*, an endangered endemic of China using ISSR markers. Biochem. Genet. 44: 29-43.

Hojjati, F., **R.P. Adams** and R. G. Terry. 2019. Discovery of chloroplast capture in Juniperus excelsa complex by multi-locus phylogeny. Phytotaxa doi.org/10.11646/phytotaxa.413.1.2.

Li, J-L., R. I. Milne, D. Ru, J-B. Miao, W-J. Tao, L. Zhang, J-Q. Liu and K-S., Mao. 2020. Allopatric divergence and hybridization within *Cupressus chengiana* (Cupressaceae), a threatened conifer in the northern Hengduan Mountains of western China. Molec. Ecol. 2020; 99:1-17. DOI: 10.111/mec.15407.

Pierre-Leandri, C., F. Xavier, L. Lizzani-Cuvelier, A. Loiseau, M. Andr, R. Fellous, J. Garnero and C. A. Oli. 2003. Chemical composition of cypress essential oils: volatile constituents of leaf oils from seven cultivated *Cupressus* species. J. Ess. Oil Res. 15: 242-247.

Steel, R. G. D. and J. H. Torrie. 1960. Principles and procedures of statistics. McGraw-Hill Book Co. New York.

Veldman D. J. 1967. Fortran programming for the behavioral sciences. Holt, Rinehart and Winston Publ., NY.

Xu, T-T, Q. Wang, M. S. Olson, Z-H. Li, N. Miao and K-S. Mao. 2017. Allopatric divergence, demographic history, and conservation implications of an endangered conifer *Cupressus chengiana* in the eastern Qinghai-Tibet Plateau. Tree Genetics Genomes 13:100, DOI 10.1007/s11295-017-1183-3 (16 p.)

Li, Yao, Liu Xia, Yang Wei and Pan Ming. 2005. Essential oil from four populations of *Cupressus chengiana*. Tianran Chanwu Yanjiu Yu Kaifa 17: 610-613.

Table 1. Compositions of the leaf oils of *Cupressus chengiana* from three populations: DDH Avg. oil (15876) = 15732,35,36,37,39,15743(6). MRJ Avg. oil (15829) = 15744-15753(10). BLJ Avg. oil (15879) = 14655, 57,58,59, 15761-65(9). Individuals D7(15738) and D9(15740) grouped with BLJ oil by MSN (Fig. 3) and B3(15756) and b7(15760) were unusual oils that are not similar to any oils (MSN, Fig. x). Shading: High values (yellow), medium (blue), low (green). Gold is very unusual high conc. and turquoise is very unusual low conc.

		Avg.	Avg.	oils like BLJ		Avg.	unusual BLJ oils		
KI	compound	MJR, Sichuan 15829	DDH, Sichuan 15876	DDH-D7 15738	DDH-D9 15740	BLJ, Gansu 15879	BLJ-B3 15756	BLJ-B7 15760	Cool et al.[1] Gansu
921	tricyclene	t	t	t	t	t	t	t	
924	α-thujene	0.6	0.6	1.3	1.1	1.1	0.1	0.5	0.9
932	α-pinene	18.5	14.1	6.4	4.5	6.3	3.7	5.5	5.8
946	camphene	0.3	t	t	t	t	t	0.1	
969	sabinene	6.0	11.3	28.8	35.7	24.5	1.0	9.3	24.9
974	β-pinene	0.6	0.4	0.2	t	0.2	0.2	0.2	0.1
988	myrcene	3.1	2.6	2.3	2.2	2.3	0.6	1.4	2.8
1002	α-phellandrene	0.1	0.1	0.1	t	t	t	t	
1008	δ-3-carene	t	t	-	-	t	t	t	
1014	α-terpinene	0.8	1.0	1.8	1.5	1.3	0.1	0.5	0.2
1020	p-cymene	0.2	0.2	0.5	0.2	0.2	t	0.1	0.1
1024	limonene	3.4	1.2	1.1	0.6	1.4	0.9	0.8	2.2
1025	β-phellandrene	3.4	2.7	1.7	0.8	1.4	0.6	0.8	1.0
1044	(E)-β-ocimene	0.2	t	0.1	t	t	t	t	
1054	γ-terpinene	1.3	1.6	2.9	2.5	2.3	0.3	0.9	0.3
1065	cis-sabinene hydrate	0.2	0.4	1.2	1.2	0.8	0.1	0.4	0.4
1086	terpinolene	2.7	1.9	1.6	1.3	1.6	0.5	0.8	1.1
1097	trans-sabinene hydrate	0.6	0.4	0.7	0.7	1.0	0.5	0.9	0.1
1097	linalool	0.6	0.5	0.7	0.7	0.9	0.5	1.1	1.3
1117	4-methoxy thujone	0.1	0.1	0.2	0.2	0.4	t	0.2	
1118	cis-p-menth-2-en-1-ol	0.1	0.3	0.6	0.5	0.4	t	0.2	
1122	α-campholenal	t	t	t	t	t	t	t	
1136	trans-p-menth-2-en-1-ol	0.2	0.2	0.4	0.3	0.2	0.1	0.1	
1145	camphene hydrate	0.3	0.3	t	t	t	0.3	0.4	
154	karahanaenone	t	t	t	t	0.1	0.1	0.1	0.2
1165	borneol	0.2	t	t	t	t	t	t	
1167	umbellulone	3.2	4.1	3.2	t	0.8	t	t	0.3
1174	terpinen-4-ol	2.1	3.8	6.6	6.2	5.1	1.0	2.0	0.5
1189	p-cymen-8-ol	t	t	0.2	t	t	t	t	
1186	α-terpineol	0.3	0.4	0.4	0.3	0.4	0.2	0.1	t
1195	cis-piperitol	t	t	0.2	0.2	t	t	t	
1207	trans-piperitol	t	0.1	0.3	0.2	0.2	t	t	
1232	thymol, methyl ether	t	t	t	-	t	t	t	
1241	carvacrol, methyl ether	t	t	t	-	t	t	t	
1249	piperitone	t	t	0.1	t	t	t	t	
1254	linalyl acetate	-	-	-	-	t	t	t	0.2
1287	bornyl acetate	0.5	0.5	t	t	0.2	0.7	0.6	0.1
1298	carvacrol	t	t	t	t	t	t	t	
1345	α-terpinyl acetate	1.0	0.5	0.7	0.3	1.1	1.0	1.1	0.9
1417	(E)-caryophyllene	0.8	0.3	0.3	0.2	0.2	0.3	0.2	0.5
1429	cis-thujopsene	t	0.4	1.4	0.2	1.0	1.9	1.1	1.2
1435	cis-muurola-3,5-diene	1.9	t	t	3.8	0.6	t	1.9	0.6
1452	α-humulene	0.4	t	t	t	0.2	0.4	0.2	0.2
1465	cis-muurola-4(14),5-diene	4.6	0.3	0.2	9.8	1.5	0.2	4.5	1.8
1478	γ-muurolene	0.2	0.5	0.5	t	0.2	0.3	0.2	
1480	germacrene D	2.0	0.7	0.5	0.6	0.6	0.6	1.4	2.5
1493	trans-muurola-4(14), 5-diene	0.2	0.3	0.2	t	t	0.2	t	
1501	epi-zonarene	1.1	t	t	t	0.3	t	t	0.2
1500	α-muurolene	0.3	1.2	0.9	2.2	0.3	0.7	0.9	

		Avg.	Avg.	oils like BLJ		Avg.	unusual BLJ oils		
KI	compound	MJR, Sichuan 15829	DDH, Sichuan 15876	DDH-D7 15738	DDH-D9 15740	BLJ, Gansu 15879	BLJ-B3 15756	BLJ-B7 15760	Cool et al.1998 Gansu
1513	γ-cadinene	0.7	1.7	1.3	t	0.4	0.6	0.6	t
1522	δ-cadinene	2.0	4.4	3.3	0.7	1.2	1.8	0.6	t
1533	10-epi-cubebol	0.3	0.2	t	t	0.2	t	t	0.4
1533	trans-cadina-1,4-diene	t	t	t	t	t	t	t	
1537	α-cadinene	t	0.4	0.3	0.9	t	t	t	
1549	elemol + hedycaryol (1:6)	1.8	3.0	4.8	4.3	11.5	14.1	14.8	14.5
1559	cis-muurola-5-en-4-α-ol	0.3	t	t	1.7	0.2	t	0.7	0.5
1574	germacrene D-4-ol	0.5	2.9	4.3	t	0.8	1.1	t	0.2
1600	cedrol	0.2	0.1	0.4	t	0.3	1.1	0.5	0.2
1607	β-oplopenone	t	0.2	0.4	0.3	t	0.8	0.4	
1618	(1,10)-di-epi-cubenol	0.2	t	t	t	t	t	t	
1630	γ-eudesmol	0.3	0.6	1.2	0.8	1.8	4.3	2.7	
1638	epi-α-cadinol	0.6	1.8	1.1	0.3	0.5	1.2	0.4	
1638	epi-α-muurolol	0.6	1.9	1.2	0.3	0.5	1.3	0.5	
1644	α-muurolol	0.2	0.7	0.4	t	t	t	t	
1649	β-eudesmol	0.5	1.2	2.0	1.4	3.8	9.0	5.4	0.3
1652	α-eudesmol	0.6	1.6	2.1	1.2	3.2	7.8	3.6	0.6
1653	α-cadinol	1.6	3.5	1.7	0.8	0.4	t	-	
1675	cadalene	t	0.2	0.4	0.2	0.8	0.8	0.7	
1958	isopimara-8(14),15-diene	0.7	0.5	t	t	0.1	0.5	0.4	
2009	manool oxide	0.2	0.1	t	0.1	0.3	0.3	1.5	0.1
2055	abietatriene	1.4	1.5	0.2	0.4	0.6	1.0	1.0	0.2
2087	abietadiene	0.5	1.2	0.3	0.5	0.5	0.8	0.3	1.2
2105	abienol, iso-, FW 290	5.3	8.8	1.8	1.6	3.1	4.2	9.6	(3.1)
2132	nezukol	-	-	-	-	-	-	-	0.2
2184	sandaracopimarinal	0.2	t	-	-	t	0.5	0.2	
2208	cis-totarol, methyl ether	0.7	1.0	t	0.3	0.3	0.8	0.5	0.1
2237	trans-totarol, methyl ether	1.2	0.7	0.2	0.4	0.7	1.3	1.2	
2269	sandaracopimarinol	t	t	t	-	0.2	0.6	0.2	
2282	sempervirol	1.0	0.7	t	0.3	0.8	2.0	1.0	2.4
2314	trans-totarol	9.6	5.3	1.0	1.9	5.8	16.8	7.8	11.7
2331	trans-ferruginol	0.3	0.3	t	t	0.2	0.3	0.1	0.6
2341	diterpene, 301,205,219, FW316	0.8	0.4	t	0.2	0.4	0.9	0.6	0.7
2364	diterpene, 190,175,277, FW316	1.0	0.5	t	0.2	0.6	1.8	0.8	0.9
2432	diterpene, 285,189,203, FW316	0.5	0.3	t	t	0.3	0.9	0.4	

KI = Kovat's Index (linear by temperature programming) om J & W DB-5 column. Values less than 0.05% are denoted as traces (t). Unidentified components less than 0.5% are not reported.

Table 2. Correlation among 15 major terpenoids. APN = α-pinene, SBN = sabinene, MYR = myrcene, GTR = γ-terpinene, TRP = terpinolene, UMB = umbellulone, 4TR = terpinen-4-ol, GCD = γ-cadinene, DCD = γ-cadinene, ELO = elemol (+ hedycaryol), BUD = β-eudesmol, IAB = iso-abienol, TME = trans-totarol, methyl ether, TTTL = trans-totarol, GR4 = germacrene D-4-ol.

	APN	SBN	MYR	GTR	TRP	UMB	4TR	GCD	DCD	ELO	BUD	IAB	TME	TTL	GR4
APN	1.00	-.67	.62	-.47	.59	.35	-.62	.21	.18	-.57	-.56	.46	.44	.22	-.15
SBN	-.67	1.00	-.24	0.83	-.36	-.31	.91	-.12	-.13	.22	.08	.-.50	-.76	-.66	.19
MYR	.62	-.24	1.00	.06	.80	.57	-.15	.26	.28	-.81	-.83	.25	.22	-.05	-.04
GTR	-.47	.83	.06	1.00	-.11	-.08	.94	-.06	.02	-.04	-.13	-.43	-.62	-.62	.18
TRP	.59	-.36	.80	-.11	1.00	.42	-.29	.24	.25	-.65	-.65	.22	.34	.07	-.08
UMB	.35	-.31	.57	-.08	.42	1.00	-.12	.40	.47	-.60	-.54	.30	.13	-.08	.33
4TR	-.62	.91	-.15	.94	-.29	-.12	1.00	-.03	.02	.12	.04	-.50	-.72	-.69	.28
GCD	.21	-.12	.26	-.06	.24	.40	-.03	1.00	.92	-.41	-.39	.31	-.14	-.36	.74
DCD	.18	-.13	.28	.02	.25	.47	.02	.92	1.00	-.48	-.44	.26	-.08	-.27	.81
ELO	-.57	.22	-.81	-.04	-.65	-.60	.12	-.41	-.48	1.00	.92	-.35	-.24	.01	-.16
BUD	-.56	.08	-.83	-.13	-.65	-.54	.04	-.39	-.44	.92	1.00	-.30	-.08	.17	-.16
IAB	.46	-.50	.25	-.43	.22	.30	-.50	.31	.26	-.35	-.30	1.00	.38	.17	.05
TME	.44	-.76	.22	-.62	.34	.13	-.72	-.14	-.08	-.24	-.08	.38	1.00	.72	-.43
TTL	.22	-.66	-.05	-.62	.07	-.08	-.69	-.36	-.27	.01	.17	.17	.72	1.00	-.48
GR4	-.15	.19	-.04	.18	-.08	.33	.28	.74	.81	-.16	-.16	.05	-.43	-.48	1.00

Table 3. Individuals, sorted by population, with unusual plants grouped with most similar population by Minimum spanning network analysis (Fig. 3) and 15 terpenoids grouped by correlation.

	4TR	GTR	SBN	APN	MYR	TRP	UMB	GCD	DCD	ELO	BUD	IAB	TTM	TTT	GR4
BLJ Bailongjiang River Gansu, 3 atypical oils: B1, B3, B7															
B1 15754	3.0	1.1	15.8	2.2	1.3	0.9	0.05	1.3	3.3	21.7	6.2	1.1	0.4	5.6	4.0
B3 15756	1.0	0.3	1.0	3.7	0.6	0.5	0.05	0.4	1.8	14.1	9.0	4.2	1.3	16.8	1.1
B7 15760	2.0	0.9	9.3	5.5	1.4	0.8	0.03	0.6	0.6	14.8	5.4	9.6	1.2	7.8	0.02
BLJ Bailongjiang River, Gansu, typical oils															
B2 15755	5.4	2.4	31.5	4.1	2.0	1.3	0.05	0.2	1.3	11.3	3.3	0.8	0.6	7.2	1.3
B5 15758	4.8	2.4	30.8	6.6	2.3	1.5	0.03	0.4	1.2	10.9	2.6	3.1	0.7	5.9	1.0
B9 15762	6.0	2.8	31.8	3.2	2.2	1.4	0.02	0.3	0.4	12.7	3.2	3.8	0.6	3.8	0.02
B11 15764	6.4	2.3	21.7	4.2	2.0	1.5	2.6	0.4	1.1	14.2	5.9	1.6	0.5	6.0	0.8
B12 15765	4.8	2.0	21.6	9.2	2.0	1.4	1.8	0.4	0.9	16.0	5.0	3.1	0.6	5.4	0.8
B6 15759	3.5	1.7	18.8	7.8	1.9	1.2	0.02	0.4	1.6	14.8	4.5	1.6	0.7	6.5	1.0
B4 15757	3.7	1.7	14.7	11.7	2.2	1.6	0.9	0.9	2.1	10.8	3.1	2.8	0.8	5.3	1.6
B8 15761	4.3	1.9	13.1	4.4	2.3	1.6	0.4	0.2	0.9	15.1	7.5	3.5	1.2	6.4	0.6
B10 15763	4.6	2.2	22.3	3.4	1.9	1.7	1.2	0.3	1.0	9.7	2.9	8.1	0.8	8.9	1.0
DDH Daduhe River, Sichuan, 6 'hybrid' oils, more similar to BLJ oils															
D9 15740	6.2	2.5	35.7	4.5	2.2	1.3	0.05	0.6	0.9	3.3	1.4	1.6	0.4	1.9	0.02
D7 15738	6.6	2.9	28.8	6.4	2.3	1.6	3.2	1.3	3.3	4.8	2.0	1.8	0.2	1.0	4.3
D11 15742	7.0	3.2	33.2	10.3	2.5	1.5	0.05	1.2	3.3	4.1	1.7	1.4	0.3	2.4	2.4
D2 15733	6.4	3.6	23.0	4.7	3.1	2.3	2.6	1.4	4.9	0.05	0.05	3.6	0.9	6.2	3.0
D3 15734	5.7	2.7	22.7	8.4	3.8	2.4	5.3	1.1	3.6	0.05	0.05	3.8	0.6	4.7	2.7
D12 15743	5.9	2.3	25.2	5.6	2.4	1.6	3.7	1.6	4.5	0.05	0.10	3.5	0.6	3.9	5.8
DDH Daduhe River, Sichuan, 6 typical oils															
D10 15741	2.8	1.4	9.8	18.5	2.6	1.8	5.0	1.5	3.9	6.2	1.8	6.3	0.20	3.7	3.4
D4 15735	2.2	1.1	7.8	17.6	2.5	1.6	0.7	1.5	3.9	6.0	2.4	10.5	1.1	5.3	2.5
D6 15737	3.9	1.5	11.5	11.6	2.2	1.7	4.3	1.8	5.3	4.9	1.4	7.9	0.8	4.2	4.0
D8 15739	4.1	1.8	14.4	8.3	2.9	2.1	8.8	1.8	4.1	3.9	2.1	5.4	1.0	3.0	3.2
D5 15736	3.4	1.6	9.0	17.2	3.1	2.0	2.7	2.4	5.5	0.05	0.2	6.0	1.2	6.1	2.7
D1 15732	4.1	2.2	15.6	14.1	2.9	2.0	3.5	1.0	3.7	0.1	0.1	11.3	0.9	6.5	2.5
MJR Minjiang River, Sichuan, lower elevation, near Gansu, typical oils															
M9 15752	1.2	0.6	0.6	25.1	2.6	2.0	2.3	0.05	0.9	7.0	2.4	2.5	1.6	10.4	0.03
M8 15751	5.1	3.1	13.3	19.4	3.1	2.7	1.4	0.4	1.3	5.2	1.5	2.9	0.8	5.1	0.10
M10 15753	3.8	2.2	14.3	9.7	3.0	2.4	4.0	0.03	1.1	3.7	1.5	3.8	1.0	8.0	0.03
M6 15749	3.2	1.8	8.8	18.3	3.1	0.6	4.4	0.4	1.4	0.4	0.4	5.5	0.9	10.4	0.4
M1 15744	1.7	1.3	8.2	18.9	3.9	2.6	3.5	0.3	1.0	0.4	0.05	6.5	1.1	8.9	0.3
M4 15747	1.0	0.6	2.7	15.7	3.3	2.9	3.2	0.2	1.3	0.5	0.05	5.3	1.4	10.1	0.2
M7 15750	1.7	1.0	2.7	17.4	2.7	2.8	3.9	0.7	3.0	0.2	0.03	4.2	1.6	10.6	0.30
M2 15745	0.8	0.5	2.8	29.6	3.2	3.0	3.3	1.4	2.7	0.05	0.02	11.8	1.0	6.2	1.7
M3 15746	1.0	0.7	2.4	18.2	3.7	2.6	4.2	1.7	3.9	0.05	0.02	9.0	1.2	9.4	1.2
M5 15748	1.4	1.1	5.2	19.6	3.7	3.8	1.8	1.7	3.5	0.03	0.02	3.7	1.0	9.7	1.2

Table 4. Individuals, sorted by sabinene concentration with unusual plants grouped with most similar population and 15 terpenoids grouped by correlation. For compound abbreviations, see Table 3.

	4TR	GTR	SBN	APN	MYR	TRP	UMB	GCD	DCD	ELO	BUD	IAB	TTM	TTT	GR4
D9 15740	6.2	2.5	35.7	4.5	2.2	1.3	0.05	0.6	0.9	3.3	1.4	1.6	0.4	1.9	0.02
D11 15742	7.0	3.2	33.2	10.3	2.5	1.5	0.05	1.2	3.3	4.1	1.7	1.4	0.3	2.4	2.4
B9 15762	6.0	2.8	31.8	3.2	2.2	1.4	0.02	0.3	0.4	12.7	3.2	3.8	0.6	3.8	0.02
B2 15755	5.4	2.4	31.5	4.1	2.0	1.3	0.05	0.2	1.3	11.3	3.3	0.8	0.6	7.2	1.3
B5 15758	4.8	2.4	30.8	6.6	2.3	1.5	0.03	0.4	1.2	10.9	2.6	3.1	0.7	5.9	1.0
D7 15738	6.6	2.9	28.8	6.4	2.3	1.6	3.2	1.3	3.3	4.8	2.0	1.8	0.2	1.0	4.3
D12 15743	5.9	2.3	25.2	5.6	2.4	1.6	3.7	1.6	4.5	0.05	0.10	3.5	0.6	3.9	5.8
D2 15733	6.4	3.6	23.0	4.7	3.1	2.3	2.6	1.4	4.9	0.05	0.05	3.6	0.9	6.2	3.0
D3 15734	5.7	2.7	22.7	8.4	3.8	2.4	5.3	1.1	3.6	0.05	0.05	3.8	0.6	4.7	2.7
B10 15763	4.6	2.2	22.3	3.4	1.9	1.7	1.2	0.3	1.0	9.7	2.9	8.1	0.8	8.9	1.0
B11 15764	6.4	2.3	21.7	4.2	2.0	1.5	2.6	0.4	1.1	14.2	5.9	1.6	0.5	6.0	0.8
B12 15765	4.8	2.0	21.6	9.2	2.0	1.4	1.8	0.4	0.9	16.0	5.0	3.1	0.6	5.4	0.8
B6 15759	3.5	1.7	18.8	7.8	1.9	1.2	0.02	0.4	1.6	14.8	4.5	1.6	0.7	6.5	1.0
B1 15754	3.0	1.1	15.8	2.2	1.3	0.9	0.05	1.3	3.3	21.7	6.2	1.1	0.4	5.6	4.0
D1 15732	4.1	2.2	15.6	14.1	2.9	2.0	3.5	1.0	3.7	0.1	0.1	11.3	0.9	6.5	2.5
B4 15757	3.7	1.7	14.7	11.7	2.2	1.6	0.9	0.9	2.1	10.8	3.1	2.8	0.8	5.3	1.6
D8 15739	4.1	1.8	14.4	8.3	2.9	2.1	8.8	1.8	4.1	3.9	2.1	5.4	1.0	3.0	3.2
M10 15753	3.8	2.2	14.3	9.7	3.0	2.4	4.0	0.03	1.1	3.7	1.5	3.8	1.0	8.0	0.03
M8 15751	5.1	3.1	13.3	19.4	3.1	2.7	1.4	0.4	1.3	5.2	1.5	2.9	0.8	5.1	0.10
B8 15761	4.3	1.9	13.1	4.4	2.3	1.6	0.4	0.2	0.9	15.1	7.5	3.5	1.2	6.4	0.6
D6 15737	3.9	1.5	11.5	11.6	2.2	1.7	4.3	1.8	5.3	4.9	1.4	7.9	0.8	4.2	4.0
D10 15741	2.8	1.4	9.8	18.5	2.6	1.8	5.0	1.5	3.9	6.2	1.8	6.3	0.20	3.7	3.4
B7 15760	2.0	0.9	9.3	5.5	1.4	0.8	0.03	0.6	0.6	14.8	5.4	9.6	1.2	7.8	0.02
D5 15736	3.4	1.6	9.0	17.2	3.1	2.0	2.7	2.4	5.5	0.05	0.2	6.0	1.2	6.1	2.7
M6 15749	3.2	1.8	8.8	18.3	3.1	0.6	4.4	0.4	1.4	0.4	0.4	5.5	0.9	10.4	0.4
M1 15744	1.7	1.3	8.2	18.9	3.9	2.6	3.5	0.3	1.0	0.4	0.05	6.5	1.1	8.9	0.3
D4 15735	2.2	1.1	7.8	17.6	2.5	1.6	0.7	1.5	3.9	6.0	2.4	10.5	1.1	5.3	2.5
M5 15748	1.4	1.1	5.2	19.6	3.7	3.8	1.8	1.7	3.5	0.03	0.02	3.7	1.0	9.7	1.2
M2 15745	0.8	0.5	2.8	29.6	3.2	3.0	3.3	1.4	2.7	0.05	0.02	11.8	1.0	6.2	1.7
M4 15747	1.0	0.6	2.7	15.7	3.3	2.9	3.2	0.2	1.3	0.5	0.05	5.3	1.4	10.1	0.2
M7 15750	1.7	1.0	2.7	17.4	2.7	2.8	3.9	0.7	3.0	0.2	0.03	4.2	1.6	10.6	0.30
M3 15746	1.0	0.7	2.4	18.2	3.7	2.6	4.2	1.7	3.9	0.05	0.02	9.0	1.2	9.4	1.2
B3 15756	1.0	0.3	1.0	3.7	0.6	0.5	0.05	0.4	1.8	14.1	9.0	4.2	1.3	16.8	1.1
M9 15752	1.2	0.6	0.6	25.1	2.6	2.0	2.3	0.05	0.9	7.0	2.4	2.5	1.6	10.4	0.03

Table 5. Individuals, sorted by elemol/ hedycaryol concentration with unusual plants grouped with most similar population and 15 terpenoids grouped by correlation. For compound abbreviations, see Table 3.

	4TR	GTR	SBN	APN	MYR	TRP	UMB	GCD	DCD	ELO	BUD	IAB	TTM	TTT	GR4
B1 15754	3.0	1.1	15.8	2.2	1.3	0.9	0.05	1.3	3.3	21.7	6.2	1.1	0.4	5.6	4.0
B12 15765	4.8	2.0	21.6	9.2	2.0	1.4	1.8	0.4	0.9	16.0	5.0	3.1	0.6	5.4	0.8
B8 15761	4.3	1.9	13.1	4.4	2.3	1.6	0.4	0.2	0.9	15.1	7.5	3.5	1.2	6.4	0.6
B6 15759	3.5	1.7	18.8	7.8	1.9	1.2	0.02	0.4	1.6	14.8	4.5	1.6	0.7	6.5	1.0
B7 15760	2.0	0.9	9.3	5.5	1.4	0.8	0.03	0.6	0.6	14.8	5.4	9.6	1.2	7.8	0.02
B11 15764	6.4	2.3	21.7	4.2	2.0	1.5	2.6	0.4	1.1	14.2	5.9	1.6	0.5	6.0	0.8
B3 15756	1.0	0.3	1.0	3.7	0.6	0.5	0.05	0.4	1.8	14.1	9.0	4.2	1.3	16.8	1.1
B9 15762	6.0	2.8	31.8	3.2	2.2	1.4	0.02	0.3	0.4	12.7	3.2	3.8	0.6	3.8	0.02
B2 15755	5.4	2.4	31.5	4.1	2.0	1.3	0.05	0.2	1.3	11.3	3.3	0.8	0.6	7.2	1.3
B5 15758	4.8	2.4	30.8	6.6	2.3	1.5	0.03	0.4	1.2	10.9	2.6	3.1	0.7	5.9	1.0
B4 15757	3.7	1.7	14.7	11.7	2.2	1.6	0.9	0.9	2.1	10.8	3.1	2.8	0.8	5.3	1.6
B10 15763	4.6	2.2	22.3	3.4	1.9	1.7	1.2	0.3	1.0	9.7	2.9	8.1	0.8	8.9	1.0
M9 15752	1.2	0.6	0.6	25.1	2.6	2.0	2.3	0.05	0.9	7.0	2.4	2.5	1.6	10.4	0.03
D10 15741	2.8	1.4	9.8	18.5	2.6	1.8	5.0	1.5	3.9	6.2	1.8	6.3	0.20	3.7	3.4
D4 15735	2.2	1.1	7.8	17.6	2.5	1.6	0.7	1.5	3.9	6.0	2.4	10.5	1.1	5.3	2.5
M8 15751	5.1	3.1	13.3	19.4	3.1	2.7	1.4	0.4	1.3	5.2	1.5	2.9	0.8	5.1	0.10
D6 15737	3.9	1.5	11.5	11.6	2.2	1.7	4.3	1.8	5.3	4.9	1.4	7.9	0.8	4.2	4.0
D7 15738	6.6	2.9	28.8	6.4	2.3	1.6	3.2	1.3	3.3	4.8	2.0	1.8	0.2	1.0	4.3
D11 15742	7.0	3.2	33.2	10.3	2.5	1.5	0.05	1.2	3.3	4.1	1.7	1.4	0.3	2.4	2.4
D8 15739	4.1	1.8	14.4	8.3	2.9	2.1	8.8	1.8	4.1	3.9	2.1	5.4	1.0	3.0	3.2
M10 15753	3.8	2.2	14.3	9.7	3.0	2.4	4.0	0.03	1.1	3.7	1.5	3.8	1.0	8.0	0.03
D9 15740	6.2	2.5	35.7	4.5	2.2	1.3	0.05	0.6	0.9	3.3	1.4	1.6	0.4	1.9	0.02
M4 15747	1.0	0.6	2.7	15.7	3.3	2.9	3.2	0.2	1.3	0.5	0.05	5.3	1.4	10.1	0.2
M6 15749	3.2	1.8	8.8	18.3	3.1	0.6	4.4	0.4	1.4	0.4	0.4	5.5	0.9	10.4	0.4
M1 15744	1.7	1.3	8.2	18.9	3.9	2.6	3.5	0.3	1.0	0.4	0.05	6.5	1.1	8.9	0.3
M7 15750	1.7	1.0	2.7	17.4	2.7	2.8	3.9	0.7	3.0	0.2	0.03	4.2	1.6	10.6	0.30
D1 15732	4.1	2.2	15.6	14.1	2.9	2.0	3.5	1.0	3.7	0.1	0.1	11.3	0.9	6.5	2.5
D12 15743	5.9	2.3	25.2	5.6	2.4	1.6	3.7	1.6	4.5	0.05	0.10	3.5	0.6	3.9	5.8
D2 15733	6.4	3.6	23.0	4.7	3.1	2.3	2.6	1.4	4.9	0.05	0.05	3.6	0.9	6.2	3.0
D3 15734	5.7	2.7	22.7	8.4	3.8	2.4	5.3	1.1	3.6	0.05	0.05	3.8	0.6	4.7	2.7
D5 15736	3.4	1.6	9.0	17.2	3.1	2.0	2.7	2.4	5.5	0.05	0.2	6.0	1.2	6.1	2.7
M2 15745	0.8	0.5	2.8	29.6	3.2	3.0	3.3	1.4	2.7	0.05	0.02	11.8	1.0	6.2	1.7
M3 15746	1.0	0.7	2.4	18.2	3.7	2.6	4.2	1.7	3.9	0.05	0.02	9.0	1.2	9.4	1.2
M5 15748	1.4	1.1	5.2	19.6	3.7	3.8	1.8	1.7	3.5	0.03	0.02	3.7	1.0	9.7	1.2

Table 6. Individuals, sorted by umbellulone (UMB) concentration with unusual plants grouped with most similar population and 15 terpenoids grouped by correlation. For compound abbreviations, see Table 3.

	4TR	GTR	SBN	APN	MYR	TRP	UMB	GCD	DCD	ELO	BUD	IAB	TTM	TTT	GR4
D8 15739	4.1	1.8	14.4	8.3	2.9	2.1	8.8	1.8	4.1	3.9	2.1	5.4	1.0	3.0	3.2
D3 15734	5.7	2.7	22.7	8.4	3.8	2.4	5.3	1.1	3.6	0.05	0.05	3.8	0.6	4.7	2.7
D10 15741	2.8	1.4	9.8	18.5	2.6	1.8	5.0	1.5	3.9	6.2	1.8	6.3	0.20	3.7	3.4
M6 15749	3.2	1.8	8.8	18.3	3.1	0.6	4.4	0.4	1.4	0.4	0.4	5.5	0.9	10.4	0.4
D6 15737	3.9	1.5	11.5	11.6	2.2	1.7	4.3	1.8	5.3	4.9	1.4	7.9	0.8	4.2	4.0
M3 15746	1.0	0.7	2.4	18.2	3.7	2.6	4.2	1.7	3.9	0.05	0.02	9.0	1.2	9.4	1.2
M10 15753	3.8	2.2	14.3	9.7	3.0	2.4	4.0	0.03	1.1	3.7	1.5	3.8	1.0	8.0	0.03
M7 15750	1.7	1.0	2.7	17.4	2.7	2.8	3.9	0.7	3.0	0.2	0.03	4.2	1.6	10.6	0.30
D12 15743	5.9	2.3	25.2	5.6	2.4	1.6	3.7	1.6	4.5	0.05	0.10	3.5	0.6	3.9	5.8
D1 15732	4.1	2.2	15.6	14.1	2.9	2.0	3.5	1.0	3.7	0.1	0.1	11.3	0.9	6.5	2.5
M1 15744	1.7	1.3	8.2	18.9	3.9	2.6	3.5	0.3	1.0	0.4	0.05	6.5	1.1	8.9	0.3
M2 15745	0.8	0.5	2.8	29.6	3.2	3.0	3.3	1.4	2.7	0.05	0.02	11.8	1.0	6.2	1.7
D7 15738	6.6	2.9	28.8	6.4	2.3	1.6	3.2	1.3	3.3	4.8	2.0	1.8	0.2	1.0	4.3
M4 15747	1.0	0.6	2.7	15.7	3.3	2.9	3.2	0.2	1.3	0.5	0.05	5.3	1.4	10.1	0.2
D5 15736	3.4	1.6	9.0	17.2	3.1	2.0	2.7	2.4	5.5	0.05	0.2	6.0	1.2	6.1	2.7
B11 15764	6.4	2.3	21.7	4.2	2.0	1.5	2.6	0.4	1.1	14.2	5.9	1.6	0.5	6.0	0.8
D2 15733	6.4	3.6	23.0	4.7	3.1	2.3	2.6	1.4	4.9	0.05	0.05	3.6	0.9	6.2	3.0
M9 15752	1.2	0.6	0.6	25.1	2.6	2.0	2.3	0.05	0.9	7.0	2.4	2.5	1.6	10.4	0.03
B12 15765	4.8	2.0	21.6	9.2	2.0	1.4	1.8	0.4	0.9	16.0	5.0	3.1	0.6	5.4	0.8
M5 15748	1.4	1.1	5.2	19.6	3.7	3.8	1.8	1.7	3.5	0.03	0.02	3.7	1.0	9.7	1.2
M8 15751	5.1	3.1	13.3	19.4	3.1	2.7	1.4	0.4	1.3	5.2	1.5	2.9	0.8	5.1	0.10
B10 15763	4.6	2.2	22.3	3.4	1.9	1.7	1.2	0.3	1.0	9.7	2.9	8.1	0.8	8.9	1.0
B4 15757	3.7	1.7	14.7	11.7	2.2	1.6	0.9	0.9	2.1	10.8	3.1	2.8	0.8	5.3	1.6
D4 15735	2.2	1.1	7.8	17.6	2.5	1.6	0.7	1.5	3.9	6.0	2.4	10.5	1.1	5.3	2.5
B8 15761	4.3	1.9	13.1	4.4	2.3	1.6	0.4	0.2	0.9	15.1	7.5	3.5	1.2	6.4	0.6
B1 15754	3.0	1.1	15.8	2.2	1.3	0.9	0.05	1.3	3.3	21.7	6.2	1.1	0.4	5.6	4.0
B3 15756	1.0	0.3	1.0	3.7	0.6	0.5	0.05	0.4	1.8	14.1	9.0	4.2	1.3	16.8	1.1
D9 15740	6.2	2.5	35.7	4.5	2.2	1.3	0.05	0.6	0.9	3.3	1.4	1.6	0.4	1.9	0.02
B2 15755	5.4	2.4	31.5	4.1	2.0	1.3	0.05	0.2	1.3	11.3	3.3	0.8	0.6	7.2	1.3
D11 15742	7.0	3.2	33.2	10.3	2.5	1.5	0.05	1.2	3.3	4.1	1.7	1.4	0.3	2.4	2.4
B7 15760	2.0	0.9	9.3	5.5	1.4	0.8	0.03	0.6	0.6	14.8	5.4	9.6	1.2	7.8	0.02
B5 15758	4.8	2.4	30.8	6.6	2.3	1.5	0.03	0.4	1.2	10.9	2.6	3.1	0.7	5.9	1.0
B9 15762	6.0	2.8	31.8	3.2	2.2	1.4	0.02	0.3	0.4	12.7	3.2	3.8	0.6	3.8	0.02
B6 15759	3.5	1.7	18.8	7.8	1.9	1.2	0.02	0.4	1.6	14.8	4.5	1.6	0.7	6.5	1.0

Table 7. Individuals, sorted by germacrene D-4-ol (GR4) concentration with unusual plants grouped with most similar population and 15 terpenoids grouped by correlation. For compound abbreviations, see Table 3.

	4TR	GTR	SBN	APN	MYR	TRP	UMB	GCD	DCD	ELO	BUD	IAB	TTM	TTT	GR4
D12 15743	5.9	2.3	25.2	5.6	2.4	1.6	3.7	1.6	4.5	0.05	0.10	3.5	0.6	3.9	5.8
D7 15738	6.6	2.9	28.8	6.4	2.3	1.6	3.2	1.3	3.3	4.8	2.0	1.8	0.2	1.0	4.3
B1 15754	3.0	1.1	15.8	2.2	1.3	0.9	0.05	1.3	3.3	21.7	6.2	1.1	0.4	5.6	4.0
D6 15737	3.9	1.5	11.5	11.6	2.2	1.7	4.3	1.8	5.3	4.9	1.4	7.9	0.8	4.2	4.0
D10 15741	2.8	1.4	9.8	18.5	2.6	1.8	5.0	1.5	3.9	6.2	1.8	6.3	0.20	3.7	3.4
D8 15739	4.1	1.8	14.4	8.3	2.9	2.1	8.8	1.8	4.1	3.9	2.1	5.4	1.0	3.0	3.2
D2 15733	6.4	3.6	23.0	4.7	3.1	2.3	2.6	1.4	4.9	0.05	0.05	3.6	0.9	6.2	3.0
D3 15734	5.7	2.7	22.7	8.4	3.8	2.4	5.3	1.1	3.6	0.05	0.05	3.8	0.6	4.7	2.7
D5 15736	3.4	1.6	9.0	17.2	3.1	2.0	2.7	2.4	5.5	0.05	0.2	6.0	1.2	6.1	2.7
D4 15735	2.2	1.1	7.8	17.6	2.5	1.6	0.7	1.5	3.9	6.0	2.4	10.5	1.1	5.3	2.5
D1 15732	4.1	2.2	15.6	14.1	2.9	2.0	3.5	1.0	3.7	0.1	0.1	11.3	0.9	6.5	2.5
D11 15742	7.0	3.2	33.2	10.3	2.5	1.5	0.05	1.2	3.3	4.1	1.7	1.4	0.3	2.4	2.4
M2 15745	0.8	0.5	2.8	29.6	3.2	3.0	3.3	1.4	2.7	0.05	0.02	11.8	1.0	6.2	1.7
B4 15757	3.7	1.7	14.7	11.7	2.2	1.6	0.9	0.9	2.1	10.8	3.1	2.8	0.8	5.3	1.6
B2 15755	5.4	2.4	31.5	4.1	2.0	1.3	0.05	0.2	1.3	11.3	3.3	0.8	0.6	7.2	1.3
M3 15746	1.0	0.7	2.4	18.2	3.7	2.6	4.2	1.7	3.9	0.05	0.02	9.0	1.2	9.4	1.2
M5 15748	1.4	1.1	5.2	19.6	3.7	3.8	1.8	1.7	3.5	0.03	0.02	3.7	1.0	9.7	1.2
B3 15756	1.0	0.3	1.0	3.7	0.6	0.5	0.05	0.4	1.8	14.1	9.0	4.2	1.3	16.8	1.1
B6 15759	3.5	1.7	18.8	7.8	1.9	1.2	0.02	0.4	1.6	14.8	4.5	1.6	0.7	6.5	1.0
B5 15758	4.8	2.4	30.8	6.6	2.3	1.5	0.03	0.4	1.2	10.9	2.6	3.1	0.7	5.9	1.0
B10 15763	4.6	2.2	22.3	3.4	1.9	1.7	1.2	0.3	1.0	9.7	2.9	8.1	0.8	8.9	1.0
B12 15765	4.8	2.0	21.6	9.2	2.0	1.4	1.8	0.4	0.9	16.0	5.0	3.1	0.6	5.4	0.8
B11 15764	6.4	2.3	21.7	4.2	2.0	1.5	2.6	0.4	1.1	14.2	5.9	1.6	0.5	6.0	0.8
B8 15761	4.3	1.9	13.1	4.4	2.3	1.6	0.4	0.2	0.9	15.1	7.5	3.5	1.2	6.4	0.6
M6 15749	3.2	1.8	8.8	18.3	3.1	0.6	4.4	0.4	1.4	0.4	0.4	5.5	0.9	10.4	0.4
M1 15744	1.7	1.3	8.2	18.9	3.9	2.6	3.5	0.3	1.0	0.4	0.05	6.5	1.1	8.9	0.3
M7 15750	1.7	1.0	2.7	17.4	2.7	2.8	3.9	0.7	3.0	0.2	0.03	4.2	1.6	10.6	0.30
M4 15747	1.0	0.6	2.7	15.7	3.3	2.9	3.2	0.2	1.3	0.5	0.05	5.3	1.4	10.1	0.2
M8 15751	5.1	3.1	13.3	19.4	3.1	2.7	1.4	0.4	1.3	5.2	1.5	2.9	0.8	5.1	0.10
M9 15752	1.2	0.6	0.6	25.1	2.6	2.0	2.3	0.05	0.9	7.0	2.4	2.5	1.6	10.4	0.03
M10 15753	3.8	2.2	14.3	9.7	3.0	2.4	4.0	0.03	1.1	3.7	1.5	3.8	1.0	8.0	0.03
B7 15760	2.0	0.9	9.3	5.5	1.4	0.8	0.03	0.6	0.6	14.8	5.4	9.6	1.2	7.8	0.02
B9 15762	6.0	2.8	31.8	3.2	2.2	1.4	0.02	0.3	0.4	12.7	3.2	3.8	0.6	3.8	0.02
D9 15740	6.2	2.5	35.7	4.5	2.2	1.3	0.05	0.6	0.9	3.3	1.4	1.6	0.4	1.9	0.02