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Composition of the Essential Oils from Underground Parts of *Valeriana officinalis* L. *s.l.* and Several Closely Related Taxa

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The volatile constituents from roots and rhizomes of *Valeriana officinalis* L. *s.l.* and of several closely related *Valeriana* taxa were investigated by GC and GC–MS (EI and NICI) analysis. Seeds were obtained from different botanical gardens in Europe, and the plants investigated were grown in an experimental field in The Netherlands. In addition, commercially available plant material of Dutch origin was investigated. Four subspecies of the collective species *V. officinalis* were included in the study. The roots and rhizomes of 16 *V. officinalis* ssp. *officinalis* samples yielded 0.22–1.55% (v/w) essential oil on a dry weight basis. Oil components present in all samples were bornyl acetate (2–36%), myrtenyl acetate (trace–9%), nojigiku acetate (trace–0.8%), valerenic acid (0.3–3%), and one as yet unidentified tertiary sesquiterpene alcohol. The oil yield for the two samples of *V. officinalis* ssp. *collina* (Wallr.) Nyman was 0.78–0.85% (v/w). The main components were bornyl acetate (22–24%), myrtenyl acetate (6–8%), camphene (4–7%), kessane (3–6%), β-eudesmol (4–5%) and a tertiary sesquiterpene alcohol (RI = 1622) amounting to 20%, which was present in one sample only. For seven samples of *V. officinalis* ssp. *sambucifolia* (Mikan f.) Celak the yield of oil was 0.19–1.57% (v/w), with main components bornyl acetate (4–25%) and valerianol (3–34%). The only sample of *V. repens* Host. yielded 0.34% (v/w) oil, with bornyl acetate (13%), valerianol (19%) and kessane (8%) as the main components. Among the other (sub)species investigated in this study, the oil of *V. celtica* L. ssp. *norica* Vierh. contained bornyl acetate (22%) and patchouli alcohol (5%). Patchouli alcohol was also present in the oil of the two samples of *V. phu* L. together with γ-patchoulene, patchoulyl acetate and a valerenal isomer (15–19%). Valeranone (16%) was the main constituent of the oil of *V. exaltata* Mikan. Bornyl acetate and valerianol were present in the essential oils of the other related valerian taxa studied. © 1997 John Wiley & Sons, Ltd.

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KEY WORDS: *Valeriana officinalis* L. *s.l.*; *Valeriana officinalis* ssp. *officinalis*; *Valeriana officinalis* ssp. *collina* (Wallr.) Nyman; *Valeriana officinalis* ssp. *sambucifolia* (Mikan f.) Celak; *Valeriana repens* Host.; *Valeriana celtica* L. ssp. *norica* Vierh.; *Valeriana angustifolia* Tausch; *Valeriana salina* Pleijel; *Valeriana tuberosa* L.; *Valeriana montana* L.; *Valeriana rossica* P. Smirnov; *Valeriana phu* L.; *Valeriana pyrenaica* L.; *Valeriana tripteris* L.; *Valeriana exaltata* Mikan; Valerianaceae; essential oil; GC–MS

INTRODUCTION

The roots and rhizomes of *Valeriana officinalis* L. *s.l.*, family Valerianaceae, are used for the preparation of phytomedicines that are employed as mild sedatives.[1,2] The plant is cultivated as a medicinal plant on a commercial scale in the northern part of Europe. The collective species *V. officinalis* L. *s.l.* is very polymorphic, with a number of naturally occurring subspecies that differ from each other by their degree of ploidy. The subspecies *V. officinalis* ssp. *officinalis* is diploid (2n = 14); it is a perennial herb with a hollow and grooved stem bearing a rosette of leaves at the base, and opposite pinnatisect leaves on the stem. The leaves comprise 11–19 lanceolate folioles, all of the same width. The subspecies is common in damp woods and meadows, as well as on dry, elevated grounds in Europe and in the temperate zones of Asia.[3] The three other subspecies investigated in this study have similar morphological characteristics.[4]

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V. officinalis ssp. *collina* (Wallr.) Nyman (2n = 28) has leaves with 15–27 folioles, all of the same width, and *V. officinalis* ssp. *sambucifolia* (Mikan f.) Celak (2n = 56; syn: *V. excelsa* Poiret) has leaves with 5–9 folioles, with the apical one clearly larger than the others. *V. repens* Host. (2n = 56; syn: *V. procurrens* Wallr.) is the fourth subspecies.[5] Often intermediates occur which are even common in certain regions; it is therefore not certain how some of the described taxa should be accommodated.[4,6]

The aim of the present study was to investigate the essential oils isolated from the underground parts of the different subspecies in order to get insight into similarities and differences as to their composition. For the same reason we investigated the essential oil content and composition of several taxa that are closely related to *V. officinalis* L. *s.l.*

EXPERIMENTAL

Plant Material

Seeds of the different subspecies of *V. officinalis* L. *s.l.*, i.e. *V. officinalis* ssp. *officinalis, V. officinalis* ssp. *collina* (Wallr.) Nyman, *V. officinalis* ssp. *sambucifolia* (Mikan f.) Celak and *V. repens* Host., and of the related taxa investigated, i.e. *V. angustifolia* Tausch, *V. salina* Pleijel, *V. tuberosa* L., *V. montana* L., *V. rossica* P. SmiRNov, *V. phu* L., *V. pyrenaica* L.

Table 1. Origin, and essential oil yield (calculated on a dry weight basis) of various valerian (sub)species

Sample plant material[a]	Origin and number	Oil yield (%, v/w)
1 *V. officinalis* polka	Rauscholzhausen [D]	1.55
2 *V. officinalis*	Unknown botanical garden	0.36
3 *V. officinalis*	VNK Elburg [NL]	0.69
4 *V. officinalis*	VNK Elburg (8570) [NL]	0.95
5 *V. officinalis*	VNK Elburg (8545) [NL]	0.83
6 *V. officinalis*	VNK Elburg (TS) [NL]	0.22
7 *V. officinalis*	VNK Elburg (TS) [NL]	0.26
8 *V. officinalis*	Botanical Garden Jena (1049) [D]	0.44
9 *V. officinalis*	Botanical Garden Jena (1093) [D]	0.31
10 *V. officinalis*	Alpengarten Belvedere Vienna (997/H10) [A]	0.34
11 *V. officinalis*	Botanical Garden Poznan [PL]	0.33
12 *V. officinalis*	Unknown botanical garden	0.65
13 *V. officinalis*	Botanical Garden Braunschweig (486) [D]	0.73
14 *V. officinalis*	Botanical Garden Göttingen [D]	1.10
15 *V. officinalis*	Ramsau am Dachstein (1988) [A]	1.18
16 *V. officinalis*	Ramsau am Dachstein (1988) [A]	1.23
17 *V. collina* (Wallr.) Nyman	Botanical Garden Stuttgart-Hohenheim (1113) [D]	0.85
18 *V. collina* (Wallr.) Nyman	Botanical Garden Stuttgart-Hohenheim [D]	0.78
19 *V. sambucifolia*	Botanical Garden Warsaw [PL]	1.24
20 *V. sambucifolia*	Botanical Garden Heidelberg [D]	1.57
21 *V. sambucifolia* Mikan F. ssp. *sambucifolia*	Botanical Garden Turku (438/117, 1988) [FIN]	1.13
22 *V. sambucifolia* Mikan F. ssp. *sambucifolia*	Botanical Garden Turku (15,117/384, 1988) [FIN]	0.20
23 *V. sambucifolia*	Unknown botanical garden (216/90)	0.45
24 *V. sambucifolia*	Botanical Garden Poznan (1944) [PL]	0.19
25 *V. sambucifolia*	Botanical Garden Budapest (147) [H]	0.21
26 *V. repens* Host.	Unknown botanical garden (787, 147/90)	0.34
Related valerian taxa		
27 *V. celtica* ssp. *norica* Vierh.	Prof. Teppner, Graz [A]	0.20
28 *V. angustifolia* Tausch	Botanical Garden Warsaw [PL]	1.10
29 *V. salina* Pleijel	Botanical Garden Leipzig [D]	0.80
30 *V. tuberosa* L.	Botanical Garden Szeged [H]	1.02
31 *V. montana* L.	Botanical Garden Jena [D]	2.20
32 *V. montana* L.	Botanical Garden Szeged [H]	1.35
33 *V. rossica* P. Smirnov	Botanical Garden Leipzig [D]	0.90
34 *V. phu* L.	Unknown botanical garden (217/90)	0.41
35 *V. phu* L.	Botanical Garden Zürich (1017/1989) [CH]	0.33
36 *V. pyrenaica* L.	Botanical Garden Zürich (1018/1989) [CH]	0.35
37 *V. tripteris* L.	Botanical Garden Jena (2944) [D]	0.38
38 *V. exaltata* Mikan	Unknown botanical garden (1987)	1.00

[a] Name as received from the botanical garden.

and *V. tripteris* L., were obtained from several botanical gardens in Europe (Table 1). Samples 1 and 38 were already available as dried underground material at the Department of Pharmaceutical Biology, Groningen; samples 15 and 16 were collected in Ramsau am Dachstein (Styre, Austria) at an altitude of 1100 m; and sample 27 was obtained as dried underground plant material from Professor Teppner (Graz, Austria). The seeds, except for samples 3–7 which were germinated at the experimental garden of the Verenigde Nederlandse Kruidencoöperatie (VNK), Elburg (The Netherlands), were germinated at the botanical garden of the University of Groningen. Subsequently, the small plants were transferred to an experimental field in Elburg. The soil consisted of sand, pH 5.6. The planting distance was 50 × 30 cm. In addition, plant material for commercial purposes (samples 3–7) was obtained from VNK. Voucher specimens have been deposited at the Department of Pharmaceutical Biology, Groningen.

Isolation Procedure

Each essential oil sample was isolated from 20.0 g of air-dried and freshly ground (1 mm) root material by hydrodistillation for 4 h in 300 ml water, according to the determination of the essential oil content in vegetable drugs, using the apparatus described in the *Nederlandse Farmacopee*, 6th edn, 2nd printing.[7] Xylene (100 µl) was used as the collection liquid, and the oil samples were stored at −20°C until analysed. The oil samples were diluted 50 times with cyclohexane prior to GC and GC–MS analysis.

Gas Chromatography

GC analysis was performed on a Hewlett Packard 5890 Series II gas chromatograph equipped with a 7673 injector and a Hewlett Packard 3365 Series II Chemstation, under the following conditions: column, WCOT fused-silica CP-Sil 5 CB (25 m × 0.32 mm i.d., film thickness 0.25 µm; Chrompack, Middelburg, The Netherlands); oven temperature programme, 50–290°C at 4°C/min; injector temperature, 250°C; detector (FID) temperature, 300°C; carrier gas, nitrogen; inlet pressure, 5 psi; linear gas velocity, 26 cm/s; split ratio, 1:56; injected volume, 1.0 µl.

Gas Chromatography–Mass Spectrometry

GC–MS (EI) was performed on a Finnigan 9500/3300/6110 GC–MS computer system. The GC conditions were: column, WCOT fused-silica CP-Sil 5 CB (25 m × 0.25 mm i.d., film thickness 0.25 µm; Chrompack); oven temperature programme, 60–300°C at 6°C/min; injector temperature 250°C; carrier gas, helium; inlet pressure, 5 psi; linear gas velocity, 30 cm/s; split ratio, 1:12. MS conditions: ionization energy, 70 eV; ion source temperature, 185°C; interface temperature, 290°C; scan speed, 1 scan/s; mass range, 34–500 u. The reactant gas mixture for negative ion chemical ionization (NICI) was CH_4–N_2O, ca 1:1.[8,9]

The identity of the components was assigned by comparison of their retention indices, relative to C_9–C_{21} *n*-alkanes, and mass spectra with corresponding data of reference compounds and from the literature.[10,11] The percentages of the components were calculated from the GC peak areas, using the normalization method.

RESULTS AND DISCUSSION

V. officinalis *L.* s.l.

The essential oil yield for the 16 samples of *V. officinalis* ssp. *officinalis* investigated varied between 0.22% and 1.55% (v/w) calculated on a dry weight basis (Table 1, samples 1–16). The well-known component of valerian oil, bornyl acetate (2–36%), was present in all of these samples (Table 2). Other components that were found in all oils were nojigiku acetate (trace–0.8%), myrtenyl acetate (trace–9%), valerenic acid (0.3–3%) and a tertiary sesquiterpene alcohol with a retention index (RI) of 1597. Other components present, but not in all samples, were the monoterpene ester myrtenyl isovalerate, the sesquiterpene hydrocarbon eudesma-2,6,8-triene, and the oxygenated sesquiterpenoids kessane, pacifigorgiol, ledol, *β*-eudesmol, valerianol, valeranone, valerenal, valerenol and *α*-kessyl acetate, as well as two unknown sesquiterpene alcohols with an RI of 1548 and 1622, respectively (Fig. 1). In only one sample (12) a pacifigorgiol isomer (RI = 1473) was detected.

According to the mass spectra, a kessanyl acetate isomer was detected in nine samples of *V. officinalis* (1–3, 6–8, 10, 11, 13), together with kessoglycyl monoacetate, that was found in four of the samples (7–10). In samples 5 and 10 faurinone was found (Fig. 1). Based on a comparison of the mass spectra of *β*-eudesmol and valerianol, and because of an abundant peak at m/z 59, it was concluded that also other tertiary sesquiterpene alcohols were present (RI = 1568, 1597, 1602, 1622, 1635). In

Table 2. Percentage composition of the essential oils isolated from roots and rhizomes of four subspecies of *V. officinalis* L. *s.l.*

Component	Retention index[a]	Sample 1–16[b]	17	18	19–25	26	M[c]	BP[d]
Tricyclene	919	tr–0.1	tr	tr	tr–0.1	tr	136	93
α-Pinene	926	0.1–2.2	0.4	0.9	0.6–2.7		136	93
Fenchene	930					0.8	136	93
Camphene	937	0.1–6.4	**4.3**	**6.9**	1.8–**8.1**	5.0	136	93
Sabinene	960	tr–0.1	tr		tr–0.9	0.1	136	93
β- Pinene	964	tr–0.9	0.3	0.7	0.2–1.2	0.6	136	93
β-Myrcene	980	tr–0.1			tr		136	43
Unknown	989	tr–0.2				0.2	144	101
α-Phellandrene	993				tr		136	93
p- Cymene	1008	0.1–1.5	0.1	0.4	0.1–1.1	0.7	134	119
1,8-Cineole	1015	tr–0.2				tr	154	43
β-Phellandrene	1016	tr–2.4	0.3	0.5	0.1–1.7	0.2	136	93
Limonene	1017	0.1–1.2			0.1–0.5	0.3	136	68
γ-Terpinene	1047	tr–0.2	tr		tr–0.2	0.1	136	93
Terpinolene	1075	tr–0.1			tr	tr	136	93
Linalol	1082	tr	tr		tr–0.2	tr	152	71
Menthenal isomer	1098	tr–0.3	0.1		0.1 –0.3	0.1	152	94
Menthenal isomer	1110	tr–0.1	0.1		tr–0.2		152	94
Camphor	1112	tr–0.1				tr	152	95
Isoborneol	1132	tr–0.1					154	95
Borneol	1140	0.1–0.6	0.4	0.7	0.2–3.0	0.7	154	95
$C_9H_{14}O$	1148	tr–0.1					138	96
Terpinen-4-ol	1154	0.1–0.6	0.1	0.3	0.1–0.9	0.2	154	71
α-Terpineol	1165	tr–0.1	tr	tr	tr–0.2	tr	152	59
Myrtenol	1171	0.1–4.0	0.6	0.2	0.1–1.3	0.6	152	79
Unknown	1173	0.1					166	135
cis-Carveol	1174	0.1–0.2			0.2–0.8		152	84
Unknown	1183	tr–0.1					166	135
trans-Carveol	1191	tr–0.1	tr		tr–0.3	tr	152	84
Cumin aldehyde	1203	tr–0.1					148	133
Thymol methyl ether	1207	tr–0.4	tr	0.3	tr–0.6	tr	164	149
Carvacrol methyl ether	1211	0.1–0.2	0.1	0.1	0.1–0.2	0.4	164	149
Thymol methyl ether isomer	1216	0.1–0.2	0.1	0.1	tr–0.2	0.2	164	149
Carvacrol methyl ether isomer	1222	tr–0.2	tr	tr			164	149
Geraniol	1233				tr		154	69
Linalyl acetate	1239				0.1		196	93
Bornyl acetate	1264	2.3–**35.5**	**23.5**	**22.2**	**4.3–25.1**	**12.7**	196	95
$C_{12}H_{20}O_2$	1268	tr–0.1					196	121
Nojigiku acetate	1272	tr–0.8	0.6	0.6	0.1–1.6	0.3	194	107
Unknown	1286	tr–0.2					162	162
Thymol	1290	0.1					150	135
Myrtenyl acetate	1299	tr–**9.1**	**5.8**	**7.9**	0.2–**7.0**	3.9	194	91
Eugenol	1305	tr–0.1					164	164
δ-Elemene	1326	0.2–2.9	1.3	0.4	0.2–4.4	0.3	204	121
Citronellyl acetate	1332	tr–0.1	tr		tr		198	81
$C_{15}H_{24}$	1340	0.1–0.3		0.5	tr–0.3	0.1	204	93
α-Ylangene	1357	0.1–0.4		0.7	tr–0.4	0.1	204	105
α-Copaene	1366	tr–0.2	0.1	0.1	tr–0.2	0.1	204	105
2,5-Dimethoxy-*p*-cymene	1372				tr–0.1		194	179
$C_{15}H_{24}$	1374	tr–1.6	tr	0.1	tr–0.2	0.1	204	147
β- Elemene	1379	0.1–0.4	0.3	0.3	0.1–0.7	0.1	204	81
$C_{15}H_{24}$	1388				0.1	0.1	204	94
$C_{15}H_{24}$	1394					0.4	204	93
$C_{15}H_{24}$	1395	0.1–1.9	0.7	1.0			204	82
2, 6-Dimethoxy-*p*-cymene	1396	0.2–1.4	0.5	0.3	0.2–0.9	1.0	194	179
$C_{15}H_{24}$	1396	0.3–1.3			0.5–2.3		204	105
$C_{15}H_{24}$	1400	tr–0.9	0.1	0.2	0.2–0.3		204	147
$C_{15}H_{24}$	1403	0.1–2.4	0.7		0.6–2.5		204	41
$C_{15}H_{24}$	1404					1.4	204	93
$C_{15}H_{24}$	1407	tr–0.1					204	105

Table 2. Continued

Component	Retention index[a]	Sample 1–16[b]	17	18	19–25	26	M[c]	BP[d]
$C_{15}H_{24}$	1418	0.1–4.7	0.1		0.1–1.6	0.1	204	161
γ-Patchoulene	1423				0.1–0.5		204	122
$C_{15}H_{24}$	1424				0.1–0.2		204	81
$C_{15}H_{24}$	1425	0.1–0.5	0.1	0.3	0.1–0.4	0.2	204	93
$C_{15}H_{24}$	1432	tr–0.1			0.1–0.2		202	91
β-Bisabolene	1439	0.2–0.8					204	69
α-Humulene	1440	0.1–0.9	0.7	0.5	0.1–3.6	0.6	204	93
$C_{15}H_{24}$	1442	tr–2.1					204	41
Eudesma-2,6,8-triene	1443	0.5–**7.6**	0.5	1.7	0.3–**5.9**	1.4	204	105
$C_{15}H_{24}$	1450	0.1–0.2	0.1		0.1–**6.5**	0.1	204	93
β-Ionone	1454	0.1–0.7	0.3		0.1–0.3		192	177
$C_{15}H_{24}$	1454	0.1–0.4					204	43
$C_{15}H_{24}$	1457				0.3–0.6		204	121
$C_{15}H_{24}$	1457					0.2	204	81
$C_{15}H_{24}$	1462	1.6				0.5	204	105
ar-Curcumene	1464	0.7–2.1	1.4	0.8	0.1–2.1	0.7	202	119
$C_{15}H_{24}$	1464	1.2					204	93
Germacrene-D	1465	0.2–1.4	0.6				204	161
$C_{15}H_{24}$	1467	0.1–1.2					204	93
α-Guaiene	1469				0.1–3.1		204	93
$C_{15}H_{24}$	1472	0.1–0.5	0.8			0.7	204	161
Pacifigorgiol isomer	1473	1.0					222	110
$C_{15}H_{24}$	1476				0.5–4.1		204	41
$C_{15}H_{24}$	1479	0.1–**4.2**	1.0		1.0–1.9	1.3	204	93
γ-Elemene	1482	0.1–0.4			0.1–0.2		204	81
$C_{15}H_{24}$	1486	0.1–0.6					204	93
$C_{15}H_{24}$	1486		0.3		0.3–0.9		204	119
$C_{15}H_{24}$	1488	0.2					204	133
$C_{15}H_{22}$	1488	0.1					202	159
$C_{15}H_{24}$	1489				0.3–1.1		204	93
α-Bulnesene	1489					0.4	204	107
$C_{15}H_{24}$	1492	0.2–0.6	0.2	0.6		0.2	204	119
Bornyl isovalerate	1492	0.5–1.2	0.9	0.4	tr–0.1	0.2	238	95
$C_{15}H_{26}O$	1494	0.6–0.8			0.5–1.2	0.7	222	69
$C_{15}H_{24}$	1495					0.2	204	93
β- Gurjunene	1498	tr–1.0	1.3		0.4–4.1	0.9	204	122
Kessane	1507	0.2–3.8	**6.3**	3.3	0.7–**8.2**	**7.8**	222	43
δ-Cadinene	1507	0.1–0.3			0.1–1.1		204	161
$C_{15}H_{24}$	1517				0.1–0.2		204	93
$C_{15}H_{26}O$	1522	**4.1–5.4**	0.4				222	59
Pacifigorgiol	1523	0.5–**3.2**		**3.0**	0.4–**2.5**	0.9	222	110
Faurinone	1526	0.4–0.6			0.3–0.9		222	43
$C_{15}H_{24}$	1527	0.3–0.8	0.4	0.5		0.5	204	93
Myrtenyl isovalerate	1535	1.6–**10.5**	1.4	1.8	0.5–2.7	3.3	236	91
$C_{15}H_{24}$	1535	0.8–**4.5**					204	121
Maaliol	1541	0.1–1.6			0.2–1.2		222	43
$C_{15}H_{24}O$	1548	0.9–**6.1**		**4.9**	0.2–2.8	0.8	220	43
$C_{15}H_{24}O$	1552	0.4–1.3				2.3	220	41
$C_{15}H_{26}O$	1555	0.2–4.2	0.8	1.4	0.2–0.7		222	121
Citronellyl isovalerate	1558	0.2–2.1	0.1	0.4	0.2–1.4	0.4	240	81
$C_{15}H_{24}O$	1561	0.1–0.6	0.2				220	43
$C_{15}H_{24}O$	1565				0.2–1.1		220	69
$C_{15}H_{26}O$	1565	0.4–0.9		0.6			222	69
$C_{15}H_{26}O$	1568	0.6–2.7	1.1			1.3	222	59
Ledol	1575	0.5–2.1	0.8	1.0	0.3–1.5	1.4	222	43
$C_{15}H_{24}O$	1578	0.1–0.5					220	93
$C_{15}H_{26}O$	1591				0.3–1.2		222	161
$C_{15}H_{26}O$	1592	0.2–1.6	0.8			0.6	222	43
$C_{15}H_{24}O$	1597				**2.2–7.5**	**4.5**	220	119

Table continues on next page

Table 2. Continued

Component	Retention index[a]	1–16[b]	17	18	Sample 19–25	26	M[c]	BP[d]
$C_{15}H_{24}O$	1597	1.4–**13.8**					220	59
$C_{15}H_{24}O$	1597		3.0	2.0			220	161
$C_{15}H_{26}O$	1602	0.2–**9.7**				0.7	222	161
$C_{15}H_{26}O$	1602				0.4–**5.1**		222	121
Unknown	1605	0.3–**10.9**	0.6				252	41
γ-Eudesmol	1605				0.5–0.7		222	161
β-Eudesmol	1613	0.6–**6.9**	3.9	**5.1**	1.9–**8.3**	**5.5**	222	59
$C_{15}H_{26}O$	1622	**14.5–15.3**	**19.5**				222	59
$C_{16}H_{28}O_2$ (isovalerate)	1623	0.3–0.4					252	57
Valerianol	1625	1.5–**14.2**		1.1	2.6–**33.9**	**19.0**	222	161
$C_{15}H_{26}O$	1626	0.2–2.1		0.9			222	43
$C_{15}H_{26}O$	1635	0.9–2.3					222	59
Valeranone	1639	0.5–**8.2**	0.8	0.5	0.2–**10.4**	1.1	222	98
Myrtenyl hexanoate	1640	0.1–0.2		0.5			250	91
Cryptofauronol	1644	0.4–3.9			0.1–2.7		238	41
$C_{15}H_{26}O$	1645	0.5–1.0	0.6	0.4	tr–0.9	0.6	222	82
$C_{15}H_{26}O$	1653	0.1–1.2					222	43
epi-α-Bisabolol	1659	0.5–1.5	0.7		0.5–1.9	0.6	222	69
$C_{17}H_{28}O_2$ (isovalerate)	1677	0.3–0.9	0.2			0.5	264	57
Valerenal	1688	0.4–**12.4**	0.5	1.6	0.3–**3.8**	0.6	218	91
$C_{15}H_{24}O$	1692					0.1	220	43
$C_{16}H_{30}O_2$ (isovalerate)	1693	0.1–0.3	0.1		0.3–3.8		254	57
Valerenol (*cis*/*trans*)	1698	0.3–1.2	0.2		0.4–1.1	0.4	220	91
Eugenyl isovalerate	1728	0.1–0.4			0.1–1.9	0.3	248	164
$C_{17}H_{28}O_2$ (acetate)	1746	1.3–**7.1**				0.5	264	75
Drimenol	1750	0.1–0.4			0.1–**4.4**		222	109
$C_{17}H_{26}O_2$ (acetate)	1768	0.4–2.6			0.3–0.8		262	43
$C_{17}H_{28}O_2$ (acetate)	1768		**2.2**			0.3	264	43
α-Kessyl acetate	1772	0.1–**12.6**			0.3–2.1		280	43
cis-Valerenyl acetate	1777	0.2–0.8		0.4	0.2–0.6	0.3	262	43
Methyl valerenate	1785	0.1–0.2					248	91
trans-Valerenyl acetate	1796	0.1–1.5			0.1–0.7		262	43
Isoeugenyl isovalerate	1814	0.1–1.1	0.3		0.1–0.9		248	164
Kessanyl acetate	1827	0.1–**3.5**	0.2	1.4			280	43
Valerenic acid	1831	0.3–2.8	0.2	0.2	0.1–**4.7**	0.1	234	91
An isovalerate	1850	tr–0.3						57
$C_{17}H_{28}O_2$ (isovalerate)	1855	0.2–0.6					264	57
$C_{17}H_{26}O_2$ (acetate)	1867	tr–**10.2**	0.2	**13.8**	tr–2.9	0.1	262	43
$C_{17}H_{32}O_3$ (Isovalerate)	1881	tr–1.1			0.1–1.5		284	57
Cryptofauronyl acetate	1890	tr–2.9	tr		tr–0.9	0.1	280	43
Methyl palmitate	1908	0.1–0.9	0.1				270	74
Eugenyl hexanoate	1917				tr–**4.9**		262	164
Palmitic acid	1946	0.1–1.9	0.2		0.1–0.3	0.3	256	60
Kessoglycyl monoacetate	1972	0.1–0.7					296	43
cis-Valerenyl isovalerate	1984	tr–0.7		0.2	tr–0.1	0.1	304	57
Ethyl palmitate	1986	tr–0.6					284	88
$C_{20}H_{34}O_2$ (isovalerate)	2004	0.1–1.1	0.1				306	57
trans-Valerenyl isovalerate	2024	tr–1.6	tr		tr–1.7	0.4	304	57
$C_{20}H_{32}O_2$ (isovalerate)	2051	tr–0.7					304	57

[a] Relative to C_9–C_{21} *n*-alkanes on the CP-Sil 5 column.
[b] tr = trace (<0.05%).
[c] M = molecular weight.
[d] bp = base peak (100%).

two samples (9 and 10) the as yet unidentified sesquiterpene alcohol with an RI of 1622 was the main component. An unidentified sesquiterpene acetate (RI = 1746) was present in some of the samples. We also found an unknown component (RI = 1148) with a molecular weight of 138. In an earlier report, two unidentified components with a molecular weight of 138 were detected in a hydrodistillate from *V. officinalis* flowers.[12] Possibly these compounds are of a comparable nature. Methyl valerenate (RI = 1785) was, as far as we know, found for the first time to be present in the essential oil of *V. officinalis* (samples 2–11). The identity of methyl valerenate was confirmed by synthesis using valerenic acid and diazomethane.[13] The compound had already been synthesized from valerenic acid in 1965,[14,15] but until now it was not reported to occur in nature.

The essential oil content of *V. officinalis* roots and rhizomes, either wild grown or cultivated, has been reported to vary from 0.1% to 2.8%.[16–19] In the monograph for *Valerianae Radix* in the European Pharmacopoeia an essential oil content of at least 0.5% is required. Both the essential oil content and its composition may strongly differ from plant to plant.[20] Also, seasonal variations play a role in the essential oil amount.[21,22] Several chemovars have been distinguished, e.g. a valerianol type, which has been wrongly called 'elemol type', and valeranone, cryptofauronol and valerenal types.[23–25]

The two samples (17 and 18) of the subspecies *collina* yielded 0.78% and 0.85% oil (v/w), which was more than the amount (about 0.3%) mentioned in the literature so far.[26] Bornyl acetate was the main component in both samples (22% and 24% respectively) which is in accordance with previous findings.[27] Myrtenyl acetate, kessane, camphene and *β*-eudesmol were main components in both samples. In sample 18 pacifigorgiol was present, but not in sample 17. Also the sesquiterpene alcohol with an RI of 1548 was only present in sample 18. The second main component in sample 17 was the sesquiterpene alcohol with an RI of 1622. The sesquiterpene acetate (RI = 1768) was only present in sample 17. Another sesquiterpene acetate (RI = 1867) was present in sample 18 in an amount of 14%, but amounted to only 0.2% in sample 17. According to the literature, large differences in the composition of the essential oil of *V. collina* exist.[27,28]

The valerian subspecies *sambucifolia* (Table 1, samples 19–25) showed a large variation in the yield (0.19–1.57%, v/w) of oil as well as in its composition, the literature also saying that large differences in the essential oil composition exist within this subspecies.[27] Bornyl acetate, together with valerianol, were the main components in all cases. In some of the samples other main components were also found, e.g. camphene (2–8%), *β*-eudesmol (2–8%), myrtenyl acetate (0.2–7%), kessane (0.7–8%) and valeranone (0.2–10%). Drimenol, which was already identified earlier as oil component of *V. dioica* and *V. edulis*,[29,30] was found in four samples (19, 21–23). A recent investigation of *V. officinalis* var. *sambucifolia* revealed 58 identified components; the main components were bornyl acetate and valerenal.[31] The latter compound was found in concentrations of 0.3–4% in the samples we analysed. We found valerianol as one of the main components (3–34%); valerenic acid was found in relatively small amounts in all samples (0.1–5%).

V. repens oil (yield 0.34%, v/w) contained bornyl acetate, kessane and valerianol as the main components. Based on the high kessane content, this subspecies seems to be chemotaxonomically closer to the valerian species occurring in Japan than to those in Europe.[32,33]

Other Valerian Taxa

The essential oil content of the roots of the related taxa, namely *V. celtica* ssp. *norica*, *V. angustifolia*, *V. salina*, *V. tuberosa*, *V. montana*, *V. rossica*, *V. phu*, *V. pyrenaica*, *V. tripteris* and *V. exaltata* (samples 27–38), varied from 0.20% to 2.20% (v/w), calculated on a dry weight basis (Table 1). Bornyl acetate was, except in samples 34–36, the main component with percentages between 6% and 46%.

From the related *Valeriana* taxa, *V. celtica* (Table 3, sample 27) is the best known species.[34] There are three subspecies, i.e. *V. celtica* ssp. *celtica* in the Alps, *V. celtica* ssp. *norica* in the eastern Alps of Austria, and *V. celtica* ssp. *pancicii* in the Montenegro area.[35] *V. celtica* ssp. *norica*, investigated in this study, is native to the 'Niedere Tauern' and to the south side of the 'Hohe Tauern' at an altitude of at least 1800 m.[4,35,36] This subspecies has been of economic importance in the region of Styria (Austria) for about 2000 years. Since the fifteenth century, the rhizomes were dug in the Alps and traded extensively in Europe for fragrance purposes.[37] We found that the main oil components were bornyl acetate, myrtenyl acetate and patchouli alcohol. The presence of bornyl acetate and patchouli alcohol is in agreement with earlier investigations.[29,30]

Also *V. phu* (samples 34 and 35) is already known for about 2000 years; it was used for medicinal purposes in the sixteenth century in the southern part of Europe.[4] So far little was known about the chemical composition of the

Table 3. Percentage composition of the essential oils isolated from roots and rhizomes of some related valerian taxa

Component	Retention index[a]	Sample													
		27[b]	28	29	30	31	32	33	34	35	36	37	38	M[c]	BP[d]
Tricyclene	919				tr	tr			tr	tr		tr		136	93
α-Pinene	926	0.1	0.1	0.4	1.2	0.7	0.4	0.1	0.4	0.4	0.5	0.3	0.2	136	93
Camphene	937	0.3	0.9	**3.7**	**4.0**	**5.9**	3.0	0.2	1.1	0.9	0.8	**9.7**	0.7	136	93
Sabinene	960			tr	0.1	0.1	0.1	tr	tr	tr	tr	0.1	0.1	136	93
β- Pinene	964	tr	0.2	0.2	0.5	0.8	0.4	tr	0.2	0.2	0.3	1.2	0.1	136	93
β-Myrcene	980					tr			tr	tr				136	43
Unknown	989								tr	0.2	tr	0.2		144	101
p-Cymene	1008		0.1	0.2	0.2	0.2	0.2	tr	0.5	0.5	1.1	0.4	0.5	134	119
1,8-Cineole	1015						0.5	tr	tr	tr	tr	tr		154	43
β- Phellandrene	1016							0.2	0.4	0.4	0.3	0.3		136	93
Limonene	1017			0.3	0.7	0.7	0.4	tr				0.4		136	68
γ-Terpinene	1047				tr	tr	tr	tr			0.1	0.1	tr	136	93
Terpinolene	1075				0.1	0.1	tr				0.1	tr	tr	136	93
Linalol	1082			tr				tr				tr	0.1	154	71
Menthenal isomer	1098			tr	tr	tr		0.1				0.1		152	94
Camphor	1112		0.2			tr		tr				0.1		152	95
Isoborneol	1132											0.1		154	95
Borneol	1140	0.5	1.2	0.4	0.5	0.2	0.2	0.3	tr	tr	0.2	0.9	0.5	154	95
$C_9H_{14}O$	1148			tr										138	96
Terpinen-4-ol	1154			0.2	0.3	0.2	0.2	0.4	0.1	0.1	0.2	0.3	0.1	154	71
Myrtenol isomer	1160		0.2	0.2	tr	tr						tr		152	79
α-Terpineol	1165				tr	tr		tr	tr	tr	tr	tr		152	71
Myrtenol	1171			0.2	0.5	0.3	0.3					1.5		152	79
cis-Carveol	1174							0.1	0.2	0.2	0.6			152	84
trans-Carveol	1191										tr	tr		152	84
Thymol methyl ether	1207			tr	0.2	tr	0.1	0.3			tr			164	149
Carvacrol methyl ether	1211			0.2	0.2	0.3	0.1	0.2			tr			164	149
Thymol methyl ether isomer	1216			0.1	0.1	0.3	0.2	0.2			tr			164	149
Carvacrol methyl ether isomer	1222			tr								0.1		164	149
Bornyl acetate	1264	**22.1**	**46.2**	**13.5**	**11.7**	**23.4**	**19.4**	**10.1**	0.9	0.9	2.3	**22.5**	**5.9**	196	95
Nojigiku acetate	1272	0.5	0.8	0.6	0.3	0.6	0.6	0.1	tr	0.1	0.1	0.3	tr	194	107
Myrtenyl acetate	1299	**3.0**	**5.7**	**5.8**	**3.5**	**9.9**	**7.5**	0.3	0.1	tr	0.1	**4.9**	0.5	194	91
δ-Elemene	1326	0.3	0.5	0.6	1.9	1.6	1.0	1.7	0.1	0.1	0.5	0.3	0.8	204	121
Citronellyl acetate	1332					0.3	0.1						0.1	198	81
$C_{15}H_{24}$	1340		0.2	0.5	0.2	0.1	0.2	0.2	tr	tr	0.1	tr	0.4	204	93
α-Ylangene	1357				0.1				0.1	0.1	tr	tr		204	105
α-Copaene	1366				tr	0.1	tr	0.1	0.1	0.1		0.1		204	105
$C_{15}H_{24}$	1369					tr		0.1	0.7	0.6				204	105
2,5-Dimethoxy-*p*-cymene	1372		0.1			tr		0.1						194	179
$C_{15}H_{24}$	1374				0.1		0.2	0.1			0.3		0.3	204	105
β-Elemene	1379			0.2	0.3	0.4	0.2	0.5	0.1	0.1	0.1	0.1	0.2	204	81
$C_{15}H_{24}$	1388							tr					0.9	204	94
$C_{15}H_{22}$	1389								0.8	0.9				202	159
$C_{15}H_{24}$	1394				0.8	0.4	1.1				0.3			204	93
$C_{15}H_{24}$	1395			0.9	0.5								2.7	204	82
2,6-Dimethoxy-*p*-cymene	1396		0.9	0.5							0.3			194	179
Longifolene	1398								0.7	0.7	0.2			204	105
$C_{15}H_{24}$	1400				0.2			1.5			0.5			204	147
$C_{15}H_{24}$	1404				1.1	1.5	1.6	2.0	0.2	0.2	1.3	2.2	1.3	204	93
$C_{15}H_{24}$	1407												0.1	204	105
α-Santalene	1409				0.1				0.2	0.2				204	94
$C_{15}H_{24}$	1418				2.6	0.1	0.2	1.3	**5.5**	**4.4**	0.2	0.1		204	161
$C_{15}H_{24}$	1418					0.1								204	121
γ-Patchoulene	1423	1.7							**4.5**	**4.9**	0.2			204	122
$C_{15}H_{24}$	1424						0.2						0.3	204	81
$C_{15}H_{24}$	1425			0.3	0.2	0.2		0.3				0.1		204	93
$C_{15}H_{24}$	1432		0.3		0.1		tr	0.1	0.4	0.5				204	69
$C_{15}H_{24}$	1433			0.2							0.1			202	91
$C_{15}H_{24}$	1439			0.3					0.2	0.1	0.7			202	91
α-Humulene	1440				0.3	0.9		0.4				0.6	0.3	204	93

Table 3. Continued

Component	Retention index[a]	Sample													
		27[b]	28	29	30	31	32	33	34	35	36	37	38	M[c]	BP[d]
$C_{15}H_{24}$	1442								3.0	3.0				204	41
$C_{15}H_{24}$	1443				0.2		**8.0**		0.2	0.1			0.1	204	105
$C_{15}H_{24}$	1443								0.5	0.5				204	107
$C_{15}H_{24}$	1444		0.8			0.3						0.3		204	69
$C_{15}H_{24}$	1445			1.4	**6.4**			**6.7**			2.9		**10.9**	204	105
$C_{15}H_{24}$	1450					0.1						0.2		204	93
$C_{15}H_{24}$	1450				0.3		0.1	0.4						204	91
$C_{15}H_{24}$	1451								0.2	0.1				202	159
β-Ionone	1454			tr	0.3	0.5	0.5	0.6				0.1		192	177
$C_{15}H_{24}$	1454			0.2								0.1		204	43
$C_{15}H_{24}$	1457								0.1	0.1	0.3		0.1	204	81
$C_{15}H_{24}$	1462								1.2	0.9				204	105
ar-Curcumene	1464	0.3	0.6	0.7	tr	2.2	1.3	tr			0.7	1.6	0.8	202	119
Germacrene-D	1465				1.8			3.0						204	161
α-Guaiene	1469							0.1	0.1	0.1	0.1			204	93
$C_{15}H_{24}$	1471		0.3	0.4					0.4					204	69
$C_{15}H_{24}$	1472										0.3			204	161
$C_{15}H_{24}$	1473			0.1	0.2	0.9				0.4		0.4		204	119
$C_{15}H_{24}$	1473			0.1				0.5						204	105
Pacifigorgiol isomer	1473				0.4		0.5						1.3	222	110
$C_{15}H_{24}$	1476			0.3		1.3					0.3	1.1		204	161
$C_{15}H_{24}$	1479				3.0			1.7	0.1	0.2	0.4		1.8	204	93
$C_{15}H_{24}$	1479					1.0	2.8		0.3	0.3				204	161
γ-Elemene	1482								0.4	0.4				204	81
$C_{15}H_{24}$	1486				0.2	0.5	0.2	0.3				0.2	0.2	204	93
α-Bulnesene	1489	0.4	0.9	0.3	0.3		0.1	0.3	0.7	0.5	0.2			204	107
$C_{15}H_{24}$	1492		0.4				0.6			0.2				204	119
Bornyl isovalerate	1492	0.1	0.2	0.1	0.1	0.5	0.4	0.2	0.1	0.1	0.1	0.1	0.5	238	95
$C_{15}H_{26}O$	1494	0.2	0.6	0.3	0.5	1.0		0.3	0.2	0.2	0.4	0.4	0.5	222	69
$C_{15}H_{24}$	1495		0.3	0.1	0.2	0.4		0.1		0.1	0.2	0.3	0.2	204	93
β-Gurjunene	1498			0.1	0.2	1.3	0.2		0.9	0.9	0.6	0.7	0.4	204	122
$C_{15}H_{24}O$	1501		tr	0.2	0.1			0.2						220	147
Kessane	1507				1.0	0.2	0.9	0.4		0.3	0.4		0.6	222	43
δ- Cadinene	1507								0.4			0.5		204	161
$C_{15}H_{26}O$	1521							0.5						222	93
$C_{15}H_{26}O$	1522	0.7	1.3			0.8			0.6	0.6		2.4		222	59
Pacifigorgiol	1523			2.6	1.0		1.1	1.3			2.6		2.1	222	110
Faurinone	1526						0.3						0.2	222	43
$C_{15}H_{24}$	1527				0.6	0.6		0.3	0.2	0.2	0.3	0.5	0.5	204	93
Myrtenyl isovalerate	1535	1.1	2.3	**3.9**	2.7		1.6		0.2			3.0	0.9	236	91
$C_{15}H_{24}$	1535					1.3		2.1	0.2	0.3	0.6		0.9	204	121
$C_{15}H_{26}O$	1536												1.8	222	123
$C_{15}H_{26}O$	1541				**7.2**		0.5	2.1						220	43
Maaliol	1541					tr			0.9	1.1				222	43
$C_{15}H_{26}O$	1548	0.8	1.3	**3.9**	1.1		1.1	2.0	2.1	2.1	2.7	0.2	**5.3**	220	91
$C_{15}H_{24}O$	1552	1.0		2.3		0.9	1.3	0.4	0.7	0.7	1.2	2.0		220	41
$C_{15}H_{26}O$	1555		2.6		0.7								2.0	222	121
$C_{15}H_{22}O$	1556								1.6	1.6		0.4		218	91
Citronellyl isovalerate	1558			2.1	0.3	0.1	0.3	0.6			2.7		0.6	240	81
$C_{15}H_{24}O$	1564								2.0	1.5		0.2		220	41
$C_{15}H_{26}O$	1565			1.0	0.5			0.8	2.4	2.4	0.8	0.3	0.6	222	69
$C_{15}H_{26}O$	1568					3.0	1.6						0.9	222	59
Ledol	1575	0.6	0.6	1.7	0.7	0.6	0.9	0.9	2.4		1.6	0.7	1.0	222	43
$C_{15}H_{24}O$	1578					0.6				2.3				220	93
$C_{15}H_{24}O$	1591						0.4						0.5	220	135
$C_{15}H_{26}O$	1592			0.4	0.5	0.6		1.4	**5.8**	2.0	0.8	0.4		222	43
$C_{15}H_{24}O$	1597	0.3	0.5	2.1	**4.0**	3.0	2.5	**9.3**			2.8	**5.0**		220	119
Bornyl hexanoate	1600										0.5			252	95
$C_{15}H_{26}O$	1602			0.8	0.3						2.5	2.2		220	43

Table continues on next page

Table 3. Continued

Component	Retention index[a]	27[b]	28	29	30	31	32	33	34	35	36	37	38	M	BP[d]
								Sample							
$C_{15}H_{22}$	1603				0.2			0.1					0.1	202	159
$C_{15}H_{26}O$	1604								0.3				1.3	222	121
$C_{15}H_{26}O$	1604								0.4	0.4				222	43
$C_{15}H_{24}O$	1605				0.5	0.8	0.7	0.7					0.8	220	69
γ-Eudesmol	1605												1.5	222	161
β-Eudesmol	1613	0.6	0.8	**6.3**	1.0	3.2	1.6	**6.8**		0.5	**7.9**			222	59
$C_{15}H_{26}O$	1617	0.4	1.0						1.0	0.6		2.7		222	43
Valerianol	1625		3.0	**13.9**	3.2	**15.6**	2.8	**13.6**			**19.9**	**11.5**	2.1	222	161
Patchouli alcohol	1625	**5.4**							**6.0**	**8.6**				222	83
$C_{15}H_{26}O$	1635					0.7						0.8		222	59
Valeranone	1639	1.2	0.4		2.5		3.3	0.7	1.0	0.8	2.5	0.5	**16.4**	222	98
Myrtenyl hexanoate	1640			0.6										250	91
$C_{15}H_{26}O$	1645		0.5	0.5	0.5	0.6	0.5	0.8			1.0	0.8	0.7	222	82
epi-α-Bisabolol	1659	0.2	0.2	0.3	0.6	0.8	1.0	0.7			1.7	0.8	**7.4**	222	69
$C_{15}H_{24}O$	1674								2.3	1.9				220	43
$C_{17}H_{28}O_2$ (isovalerate)	1677	0.7	1.5	1.1	0.6	0.3	0.5	0.6			0.9	0.4	0.2	264	57
Valerenal	1688		0.2	0.2	**4.5**		**8.8**	3.7			3.5	0.4	**4.7**	218	91
$C_{15}H_{24}O$	1692	0.4	0.8	0.2		0.1		0.2	0.8	0.8	0.2	0.1	0.2	220	43
Valerenol (*cis*/*trans*)	1698				0.6		1.1	0.4			1.6	0.2	1.4	220	91
Valerenal isomer	1701								**14.8**	**18.5**				218	91
Eugenyl isovalerate	1728	0.9	1.5	1.3	0.1		0.3	0.3			0.3	0.4		248	164
$C_{17}H_{28}O_2$ (acetate)	1746								0.2	0.2	3.2			264	75
Drimenol	1750	1.1	2.4	0.9					0.5	0.6				222	109
$C_{17}H_{26}O_2$ (acetate)	1768				1.5	0.6	0.6	1.9		0.5	0.2	0.5		264	43
α-Kessyl acetate	1772					0.1	0.2					0.2		280	43
cis-Valerenyl acetate	1777		0.3		0.5		0.4	0.6	1.3	0.9	0.6		0.6	262	43
trans-Valerenyl acetate	1796				0.7		0.4	0.8	0.2				0.5	262	43
Isoeugenyl isovalerate	1814	0.3	0.7	2.5	1.0	0.2		1.0			0.2		0.3	248	164
Kessanyl acetate	1827	0.7		1.2	2.3	0.2	1.8		0.1	0.1				280	43
Valerenic acid	1831	0.3	0.3		1.1				1.0	1.2		0.5	0.6	234	91
$C_{17}H_{26}O_2$ (acetate)	1867	0.3	0.6	0.7	2.8		3.2	0.2	0.6	0.4	0.9	0.1		262	43
$C_{17}H_{32}O_3$ (isovalerate)	1881		0.4	0.9							1.2			284	57
Cryptofauronyl acetate	1890		0.4		0.1	0.1	0.1	0.1	0.1	0.1	0.9	0.2	0.6	280	43
Palmetic acid	1946		0.6	0.4	0.2		0.3	0.2	0.1	0.1	0.2	0.1	0.2	256	60
cis-Valerenyl isovalerate	1984				0.2	tr	0.5	0.2			0.1	0.1	0.2	304	57
Patchoulyl acetate	2001								**3.3**	**3.1**				264	43
trans-Valerenyl isovalerate	2024				0.7		0.5	0.4	0.1	0.1	1.9	0.1	1.8	304	57

[a] Relative to C_9–C_{21} *n*-alkanes on the CP-Sil 5 column.
[b] tr = trace (<0.05%).
[c] M = molecular weight.
[d] BP = base peak (100%).

essential oil. In the samples we analysed, bornyl acetate was only present in small amounts, whereas a sesquiterpene hydrocarbon (RI = 1418), γ-patchoulene, patchouli alcohol, a valerenal isomer (RI = 1701) and patchoulyl acetate, together with some unknown oxygen-containing sesquiterpenes (RI = 1548, 1564, 1565, 1592, 1674) were the main components. Patchouli alcohol has been reported only once as a constituent of *V. officinalis*,[38] but it can not be excluded that the investigated commercially obtained dry roots and rhizomes in that study were from *V. phu* instead of *V. officinalis*. In view of the presence of patchouli alcohol, *V. phu* probably belongs to the subclasses to which *V. wallichii* and *V. fauriei* also belong.[39]

In *V. exaltata* (sample 38) the main components were bornyl acetate, valeranone, valerenal, a sesquiterpene hydrocarbon (RI = 1445) and two sesquiterpene alcohols (RI = 1548 and 1659). Earlier investigations on *V. exaltata* showed large differences in the composition of its oil. So far, bornyl acetate, an unknown sesquiterpene, valeranone and valerenal had been identified.[27] The published mass spectrum of that unidentified sesquiterpene shows a great similarity to the spectrum of bornyl isovalerate recorded in our study, while the published mass spectra of two unidentified sesquiterpene alcohols[27] are identical with those of β-eudesmol and valerianol.

Data on the essential oil composition of *V. angustifolia*, *V. salina*, *V. tuberosa*, *V. montana*, *V. rossica*, *V. pyrenaica* and *V. tripteris* could not be found in the literature (Table 3). Within these taxa, the largest amount of bornyl acetate (46%) was detected in the oil of *V. angustifolia* (sample 28), and the smallest amount of that of *V. pyrenaica* (sample 36). Valerianol was present in all of these samples. The largest amount of valerianol (20%) was found in the oil of *V. pyrenaica* and the smallest amount was found in one of the oils of *V. montana*. The main unidentified sesquiterpene hydrocarbons were found in *V. montana* (sample 32; RI = 1443), in *V. tuberosa* (sample 30; RI = 1445) and in *V. rossica* (sample 33; RI = 1445). Furthermore, a number of unidentified oxygen-containing sesquiterpenes were found in several samples.

Valerenic acid could be detected in most of the essential oils, but the amounts were smaller than the total content in extracts of the underground plant material as analysed by HPLC.[40,41]

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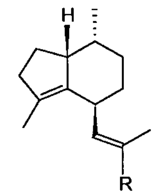
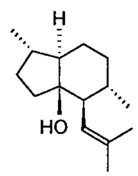
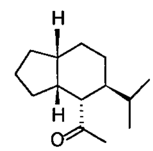
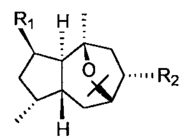


RI	R	
1688	CHO	Valerenal
1698	CH_2OH	Valerenol
1777/1796	$CH_2O\text{-}CO\text{-}CH_3$	*cis/trans*-Valerenyl acetate
1785	$COOCH_3$	Methyl valerenate
1831	COOH	Valerenic acid
1984/2024	$CH_2O\text{-}CO\text{-}CH_2\text{-}CH(CH_3)_2$	*cis/trans* Valerenyl isovalerate

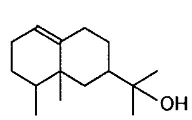


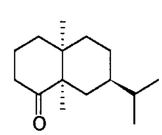


RI = 1523 Pacifigorgiol RI = 1526 Faurinone



RI	R_1	R_2	
1507	H	H	Kessane
1772	$CH_2O\text{-}CO\text{-}CH_3$	H	α-Kessyl acetate
1827	H	$CH_2O\text{-}CO\text{-}CH_3$	Kessanyl acetate
1972	$CH_2O\text{-}CO\text{-}CH_3$	OH or	
	OH	$CH_2O\text{-}CO\text{-}CH_3$	Kessoglycyl monoacetate





RI = 1625 Valerianol RI = 1639 Valeranone

Fig. 1. Structural formulae of some typical constituents of *Valeriana officinalis* L. *s.l.* and their retention indices on a CP-Sil 5 column

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