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Chemical composition of essential oils of hops (*Humulus lupulus* L.) growing wild in Aukštaitija

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Wild hop (*Humulus lupulus* L.) cones were collected in five localities of Aukštaitija. Essential oils were produced by hydrodistillation and analysed using GC and GC/MS. Different mixtures of compounds were found in volatile oils. Only two samples contained the same major constituents α-humulene (17.1–33.4%), β-bisabolol (13.1–15.0%), β-caryophyllene (6.2–9.8%) and myrcene (6.1–6.7%). The main compounds of the other three essential oils were different. One sample of oil included α-humulene (33.2%), β-caryophyllene (14.5%), α-zingiberene (5.6%) and myrcene (5.1%), the second sample contained α-humulene (14.2%), myrcene (10.5%), β-farnesene (9.5%) and β-bisabalol (9.6%) and the third one γ-elemene (14.0%), myrcene (8.5%), β-farnesene (7.8%) and α-humulene (6.6%) as major constituents. The largest part (47.8–73.5%) of the essential oils comprised sesquiterpene hydrocarbons. Three hop essential oils included 47.2–59.8% of monocyclic sesquiterpenoids and other two samples contained only 28.6–35.4% of these compounds. The constituents with five carbon skeletons (humulane, bisabolane, caryophyllane, farnezane and elemane) made up 57.6 – 70.8 % in the above three oils and 42.7–53.6% in the other two samples. Ninety eight identified constituents made up 86.1–98.8% of the essential oils.

Key words: *Humulus lupulus* L., Cannabaceae, hop cones, chemical composition of essential oils, myrcene, β-caryophyllene, γ-elemene, α-humulene, β-farnesene, β-bisabolol

INTRODUCTION

Records of brewing data go back to 7000 B. C. in Babylon and in Ancient Egypt rather later [1]. Brewers used and cultivated hops in Babylon and in some European countries. Selection of improved hop varieties has been a continuous process for the most part of the second millennium [1, 2]. The value of hops for the flavour and preservation of beer has been recognized in many countries. The Bavarian Purity Law of 1516 decreed that only hops could be used for bittering beers in Germany. Hop chemistry was investigated in the twentieth century, although some compounds had been separated earlier [1, 3]. The bittering compounds of beer were called α- and β-acids. α-Acids include humulone ($C_{21}H_{30}O_5$) and four analogues with the same functional groups and a different number of carbon atoms in one side chain. β-Acids are lupulone ($C_{26}H_{38}O_4$) and analogues. α-Acids during the wort boiling of beer are isomerised to iso-α-acids, which are much more soluble and more bitter than the parent compounds. iso-α-Acids are unstable in the sunlight. The aroma of beer packed in clear and green glass in sunlight (350–500 nm) becomes unpleasant because of the photochemical degradation of iso-α-acids. The aroma of beer is formed by hop essential oil constituents [1, 3–6] and their transformation products [7]. About a hundred constituents of hop essential oils were identified till 1964 [3]. Chromatographic analysis registered about 400 volatile compounds, but only more than 200 components have been identified [4, 5]. The main monoterpene hydrocarbon myrcene is an undesirable constituent because of its unpleasant and harsh odour. Most of monoterpene hydrocarbons are evaporated during beer boiling. The major sesquiterpene hydrocarbons of hop essential oils are α-humulene and β-caryophyllene [1, 3–7]. Some varieties of hops biosynthesize marked amounts of farnesene, selinene and bergamotene. Oxygenated sesquiterpenes of the essential oils and those formed during the brewing process were found in beer [7]. The above compounds were included in the mixture which formed the aroma and flavour of beer. All constituents of beer odour are not identified till now. At present, brewers use not only hop cones or their pellets, but also different extracts and fractions of hop essential oils. Special hop products are used in different processes of beer preparation. The main characteristics of hop cones are the amounts and chemical composition of α- and β-acids and essential oils. Hops are divided into three groups according to the above compounds: *a*) aroma hops, *b*) α-hops and *c*) dual purpose hops. The air-dry hop cones of *b* and *c* groups contain 6.0–13.0% of α-acids and 0.5–2.0% of essential oils. The content of α-acids (3.0–7.5%) is lower in aroma hops than in plant cones of other groups. The chemical composition of essential oils also differs in the above groups. The content of myrcene is higher in the oils of *b* and *c* groups than in the essential oil of aroma hops. An opposite correlation was noted for α-humulene. An important characteristic of hop essential oils is the ratio of humulene/caryophyllene content [5, 6]. This ratio for aroma hops is larger than for the other hop groups oils. The opposite correlation is determined for the ratio of selinene/caryophyllene amounts. The authors of [5] proposed that the ratio of humulene/farnezene content is suitable for characterisation of hop varieties. The above ratio in aroma hops is lower than in α-hops and dual purpose hops. The authors of [4] for characterisation of hop varietes used the principal component analysis. All above data were found mainly for cultivated hops. The search for new hop varietes is in progress [1]. Sometimes as one parent plant for a new variety local wild hop is used [1, 2]. Data on the chemical composition of wild hop essential oils will help to increase the aroma qualities of new varieties. The local brewers used wild hops in their products. Wild hops grow in different parts of Lithuania [8]. In addition to providing bitterness and aroma to beer, hops are used for medicinal, culinary and cosmetic purposes in the world [1] and in Lithuania [9–11]. Hop essential oils are used for healing of the same deseases as other hop extracts and preparations [1, 9–12]. Hop essential oils act as an aphrodisiac, they show anodyne antimicrobial, antiseptic, antispasmodic, astringent, diuretic, emollient, estrogenic, hypnotic, nervine, sedative and soporific effects [12].

Data on the constituents of essential oils will help the users to choose more accurately the hop products for healing and brewing purposes.

MATERIALS AND METHODS

Samples of wild hops (*Humulus lupulus* L.) were collected in 2003 in five localities of Aukštaitija: A – Paškonys (Utenos district), B – Karviai (Vilnius district), C – Juodgalviai (Ignalinos district), D – Mielagėnai (Ignalinos district), E – Peičupys (Ignalinos district). Voucher specimens have been deposited in the Herbarium of the Institute of Botany (BILAS numbers: A-6703, B-6710, C-6707, D-6706, E-6708). The plants were air-dried at room temperature (20–25 °C). Essential oils were prepared by hydrodistillation of 2–3 g air-dried samples.

Analyses of the essential oils were carried out by GC and GC/MS. A HP 5890II chromatograph equipped with FID and a capillary column HP-FFAP (30 m × 0.25 mm) was used for quantitative analysis. The GC oven temperature was set at 70 °C for 10 min and then programmed from 70 to 210 °C at a rate of 3 °C min^{-1} using He as a carrier gas (0.7 ml min^{-1}). The injector and detector temperatures were 200 and 250 °C, respectively. Analyses with GC/MS were performed using a gas chromatograph 5980 (Hewlett Packard) interfaced to a HP 5971 mass selective detector and HP 7673 split/splitless injector. The separation was performed on a CP-Sil 8 CB silica capillary column (50 m × 0.32 mm; film thickness 0.25 μm). The GC oven temperature was programmed as follows: from 60 °C (isothermal for 2 min) increased to 160 °C at the rate of 5 °C/min and to 250 °C at the rate of 10 °C/min and the final temperature was kept for 3 min. The temperatures of the injector and detector were 250 °C and 280 °C, respectively. The flow rate of carrier gas (helium) was 1 ml/min. Mass spectra in electron mode were generated at 70 eV.

The percentage composition of the essential oils was computed from GC peak areas without correction factors. Qualitative analysis was based on the comparison of retention times and retention indexes on both columns and the mass spectra with corresponding data in the literature [13–14] and the computer mass spectra libraries (Wiley and NBS 54K).

RESULTS AND DISCUSSION

Most of domestic brewers of Lithuania live in Aukštaitija. They use local wild hops. The aroma and flavour of beer depend on the chemical composition of hop (*Humulus lupulus* L.) essential oils. Three characteristic constituents for hop oils, α-humulene, β-caryophyllene and myrcene, were found in all oils of plant cones collected in five localities (Table). The quantity of acyclic monoterpene myrcene with unpleasant odour in the essential oils varried from 5.1 to 10.5%. The quantity of this compound in the oils under study (Table) was lower than in cultivated plants (20–50%) [5, 6]. The content of the main sesquiterpene hydrocarbon of the hop essential oils, α-humulene (6.6–33.4%), differed several times in the samples. This compound was the first major constituent in four essential oils from hops in localities A–C (Table). Only two samples, A (33.2%) and C (33.4%), contained the same quan-

Table. **Chemical composition of essential oils of hops (*Humulus lupulus* L.) growing wild in Aukštaitija**

Compounds	RI	A	B	C	D	E
1	*2*	*3*	*4*	*5*	*6*	*7*
Methyl hexanoate	905	t	0.4	t	0.4	t
α-Thujene	931	t	0.5		t	?
α-Pinene	939	t	0.3	t	t	t
β-Pinene	980		t	t		t
Myrcene	**991**	**5.1**	**6.7**	**6.1**	**10.5**	**8.5**
Butanoic acid butyl ester	993		t			t
α-Phellandrene	1003	t	t	t	t	
p-Mentha-1(7),8-diene	1004	0.2				
p-Cymene	1025	t	t	t	t	
Methyl heptanoate	1026			0.1	t	0.1
(E)–β- Ocimene	1050		0.5	t	1.0	t
Terpinolene	1089	t	1.0	0.1	1.1	t
2-Nonanone	1090		0.2		t	0.2
Linalool	1097	t	t	0.2	0.2	0.2
n-Nonanal	1101			1.1	1.8	1.0
Methyl 6-methylheptanoate	1115					0.2
Methyl octanoate	1127					0.1
n-Decanal	1220	0.5				0.1
2-Undecanone	1294		0.6	0.1	0.3	1.4
n-Tridecane	1300					0.3
Methyl geranate	1323					0.2
Methyl decanoate	1326		1.4	0.3	2.9	1.1
δ-Elemene	1339		t			0.3
α-Cubebene	1351		t			t
α-Ylangene	1375	0.6	t	0.2		0.1
α-Copaene	1376	1.5	t	0.3		0.3
l-Tridecene	1385					0.2
β-Elemene	1391	0.3				0.5
n-Tetradecane	1400	1.3				
α-Gurjunene	1409		0.4			0.5
(E)-α-Bergamotene	1413		t	0.3		
β-Caryophyllene	**1418**	**14.5**	**6.2**	**9.3**	**6.8**	**5.1**
β-Ylangene	1421					0.5
β-Gurjunene	1432	1.2	0.2	0.5	t	
γ-Elemene	1433	0.7	4.6		3.6	**14.0**
(E)-α-Bergamotene	1435	t		2.9		0.5
α-Guaiene	1438				0.7	
Aromadendrene	1439		3.2			1.5
α-Humulene	**1454**	**33.2**	**17.1**	**33.4**	**14.2**	**6.6**
(E)-β-Farnesene	**1457**		1.5		**9.5**	**7.8**
(Z)-Muurola-4(14),5-diene	1460	0.3	1.5			
Alloaromadendrene	1461	1.2	1.2	1.3	1.0	2.2
α-Acoradiene	1466			0.4		
γ-Gurjunene	1473	0.4			1.6	4.6
γ-Muurolene	1477				2.0	
2-Tridecanone	1477		0.2		1.0	0.5
γ-Curcumene	1481	0.4				
ar-Curcumene	1483	2.3		t		

tity of α-humulene as cultivated hops (20–50%) [5, 6]. These two essential oils might be called oils of α-humulene chemotype.The sample A contained β-caryophyllene (14.5%) as the second major constituent, and its chemical composition was closest to that of cultivated plant oils. The essential oil C contained β-bisabolol (15.0%) as the second major constituent. The more precise names of the essential oils if A and C chemotypes might include at least the names of the first two major compounds. β-Bisabolol was also a second main constituent in sample B. Only two essential oils, B and C, contained the same four major constituents. β-Caryophyllene and myrcene were the third or the fourth main compounds of the above essential oils (Table). The chemotype of oils B and C might be designated as α-humulene/β-bisabolol. Sesquiterpene alcohol bisabolol was not found in the essential oils of cultivated hops [3, 5, 6]. A high content of β-bisabolol (9.6%) was found in sample D. The above oil included nearly the same quantity of β-farnesene (9.5%). The essential oil E also contained 7.8% of β-farnesene, but the first major constituent of this oil was γ-elemene (14.0%). The essential oils D and E were of mixed chemotypes: D was α-humulene/myrcene/β-farnesene and E γ-elemene/myrcene/β-farnesene. The first major constituent of cultivated hops, α-humulene [1, 3–6], was only the fourth main compound of the essential oil E. The third major constituent, farnesene, of the oils D and E is characteristic of the noble hop variety 'Saaz' growing in Czechia (Bohemia). The brewers of "Kalnapilis", using

Table continued

1	2	3	4	5	6	7
β-Selinene	1490	1.9	3.0	1.7	2.0	6.2
δ-Selinene	1492	3.8	1.1	0.2	1.5	t
Muurola-4(14)-diene	1494		1.9	t		
α-Zingiberene	1495	5.6	2.6	3.6	1.6	0.7
α-Muurolene	1500		0.3	0.4		
(E)-β-Guaiene	1503			0.1		
(E, E)-α-Farnesene	1506	1.2	0.9			
β-Bisabolene	1509			0.9		0.9
γ-Cadinene	1513	1.3	1.5	1.3		1.0
(Z)-γ-Bisabolene	1515		1.9	2.1	0.7	0.6
7-epi-α-Selinene	1517					0.3
δ-Cadinene	1524	2.3	1.5	1.5	1.0	1.2
(E)-γ-Bisabolene	1531		1.2	0.3	0.7	2.2
Cadina-1(2),4-diene	1535	0.3		0.3		
α-Cadinene	1538	0.2	0.3	0.2		
α-Calacorene	1542	0.2				
Selina-3,7(11)-diene	1547		1.1	0.8	0.6	2.3
Elemol	1550			0.1		0.8
Germacrene B	1558		0.7	0.4	0.3	2.3
Caryophylene alcohol	1568		0.2	1.2		
n-Tridecanol	1575			0.1	0,5	
Germacrene-D-4-ol	1577		0.4		0.5	0.4
Spathulenol	1578		0.7	0.3	2.6	0.6
Caryophyllene oxide	1581	0.5	1.5	1.4	2.9	1.3
Globulol	1583			0.2	1.0	0.4
Viridoflorol	1590		0.7			0.4
Geranyl 2-methyl butanoate	1601				0.8	
Guaiol	1602		0.6			0.3
α-epi-7-epi-5-Eudesmol	1607		1.0			0.5
Humulene epoxide II	1608	3.3	3.0	2.8	4.7	0.5
Tetradecanal	1613			0.1	0.8	0.4
1,10-di-epi-Cubenol	1616	0.2		0.5		
(?)-Bisabolene-11-ol	1619		1.4	0.1		0.6
10-epi-γ-Eudesmol	1624		0.7		0.4	0.8
1-epi-Cubenol	1627	0.2		0.5		
Eremoligenol	1631					1.1
γ-Eudesmol	1632		0.8		0.7	0.8
β-Acorenol	1634		0.3			
Epi-α-Cadinol	1640	0.3	0.5	0.5	0,8	1.0
α-Muurolol	1645	0.1			t	
β-Eudesmol	1649	0.1	1.7	0.3	1.3	2.7
β-Eudesmol	1652		2.1	0.8	1.9	2.8
α-Cadinol	1654	0.3				
Selin-11-en-4-α-ol	1660		1.8	0.7		1.3
14-hydroxy-9-epi-(E)-Caryophyllene	1664				1.2	
Intermedeol	1667		0.7			
epi-β-Bisabolol	1672	0.4		1.3		0.7
β-Bisabolol	1675	0.1	**13.1**	**15.0**	**9.6**	1.0
n-Tetradecanol	1676				0.3	0.1
(Z)-Nerolidol acetate	1678				1.4	

the ‘Saaz’ hop variety, prepared Kalnapilis Original beer, which won the golden medal in World Beer Cup – 2004 in the Muenchener style Helles category.

The largest part of hop essential oils under study comprised sesquiterpene hydrocarbons (Table, 47.8–73.5%). Oxygenated sesquiterpenes occupied the second place. Four essential oils (B–E) contained 20.8–33.1% of the above compounds. Sample A included a lower quantity (5.6%) of oxygenated sesquiterpenes, but this essential oil contained the largest amount of sesquiterpene hydrocarbons (73.5%). The variation of sesquiterpenoid amounts was smaller (90.1–76.8 = 13.3%) than that of separate groups: hydrocarbons (73.5–47.8 = 25.7%) and oxygenated compounds (33.1–5.6 = 27.5%).

The monocyclic sesquiterpenoids with humulane (Scheme: 2, Table: α – humulene + humulene epoxide II) and bisabolane (Scheme, 3: α-curcumene + ar-curcumene + α-zingiberene + β-bisabolene + + (Z)-γ-bisabolene + (E)-γ-bisabolene + (Z)–bisabolene-11-ol + epi -β-bisabolol + β-bisabolol) carbon skeletons comprised about half (47.2–59.8%) of the essential oils A–C. The samples D and E contained smaller amounts of the above compounds (11.5–31.8%), but they included larger quantities of acyclic constituents with a farnesane (8.7–9.5%) and monocyclic compounds with an elemane (3.6–17.1%) skeleton. β-Farnesene and both farnesols are sesquiterpene hydrocarbons with a farnesane skeleton (Scheme: 1, Table). Three elemenes and elemol comprised a group of compounds with an elemane skeleton (Scheme: 4, Table). The

Table continued

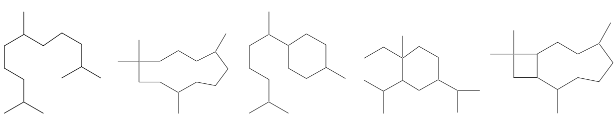
1	*2*	*3*	*4*	*5*	*6*	*7*
α-Bisabolol	1686	0.2	1.3	1.9	1.0	1.9
Eudesm-7(11)-en-4-ol	1700		0.4			
(Z, Z)-Farnesol	1718		0.3	0.2		0.8
(E, E)-Farnesol	1725			0.1		0.1
Total		86.1	98.8	98.4	96.1	97.5
Monoterpene hydrocarbons		5.3	9.0	6.2	12.6	8.5
Oxygenated monoterpenes		0.0	1.4	0.5	3.9	1.5
Aliphatic hydrocarbons		1.3	0.0	0.0	0.0	0.5
Oxygenated aliphatics		0.5	1.4	1.5	2.8	3.9
Sesquiterpene hydrocarbons		73.5	53.9	62.3	47.8	62.2
Oxygenated sesquiterpenes		5.6	33.1	27.9	29.0	20.8
Humulane skeleton (H)		36.5	21.5	36.3	18.9	7.1
Bisabolane skeleton (Bi)		11.1	20.0	23.5	12.9	4.4
Elemane skeleton (E)		1.0	5.7	0.1	3.6	17.1
Farnezane skeleton (F)		1.2	2.7	0.3	9.5	8.7
Caryophyllane skeleton (Cp)		15	7.7	10.7	10.9	6.4
Monocyclic sesquiterpenoids (H + Bi + E)		48.6	47.2	59.8	35.4	28.6
(H + Bi + E + F)		49.8	49.9	60.1	43.9	37.3
(H + Bi + E + F + Cp)		64.8	57.6	70.8	54.8	42.7

Notes. t – traces (< 0.1%). RI – retention indexes on nonpolar column. A-E – growing localities.

amounts of bicyclic and tricyclic sesquiterpenoids with eleven different carbon skeletons were markedly smaller (exept compounds with caryophyllane skeleton) than those of three above monocyclic carbon skeletons. Only three compounds, β-caryophyllene, caryophyllene oxide and 14-hydroxy-9-epi-(E)-caryophyllene, were with a caryophyllane skeleton (Scheme: 5, Table). The amount of these compounds varried from 6.4 to 15.0%. The constituents with five above carbon skeletons (Scheme) comprised 54.8–70.8% of the essential oils A–D (Table). Only the sample E contained <43% of these constituents.

Ninety eight compounds were identified from ~200 found in the essential oils. The identified constituents made up 86.1–98.8% of the oils.

The healing power and beer aroma differ using wild hops from different localities of Aukštaitija because of composition variations of the essential oils.



1 2 3 4 5

Scheme. The main carbon skeletons of sesquiterpenoids in the essential oils of hops wild growing in Aukštaitija: *1* – farnezane, *2* – humulane, *3* – bisabolane, *4* – elemane and *5* – caryophyllane

CONCLUSIONS

Wild hops biosynthesized different essential oils in five localities of Aukštaitija. Only two (B, C) samples contained the same major constituents, α-humulene (17.1–33.4%), β-bisabolol (13.1–15.0%), β-caryophyllene (6.2–9.3%) and myrcene (6.1–6.7%). The main constituents of the other three essential oils were different. One sample (A) contained α-humulene (33.2%), β-caryophyllene (14.5%) myrcene (5.1%) and α-zingiberene (5.6%), the second sample (D) contained α-humulene (14.2%), myrcene (10.5%), β-farnesene (9.5%) and β-bisabolol (9.6%) and the third one γ-elemene (14.0%), myrcene (8.5%), β- farnesene (7.8%) and α-humulene (6.6%) as the major constituents. Two essential oils containing >30% of α-humulene might be designated as oils of humulene chemotype. Both above oils contained different second main constituents. The more precise names of chemotypes of the hop essential oils could include the names of two or three major constituents.

The compounds with humulane, bisabolane, caryophyllane, farnesane and elemane carbon skeletons comprised 54.8–70.8% of the essential oils in four of five samples. The ninety eight identified constituents made up 86.1–98.8% of the oils.

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AUKŠTAITIJOJE AUGANČIŲ PAPRASTŲJŲ APYNIŲ *HUMULUS LUPULUS* L. ETERINIŲ ALIEJŲ CHEMINĖ SUDĖTIS

S a n t r a u k a

Paprastojo apynio *Humulus lupulus* L. spurgai surinkti penkiose Aukštaitijos vietovėse. Džiovinti spurgai distiliuojami vandens garais bei gauti eteriniai aliejai tiriami dujų chromatografijos ir masių spektrometrijos metodais. Gautus lakiuosius aliejus sudaro skirtingi komponentai. Tik du pavyzdžiai turi tuos pačius pagrindinius junginius: α-humuleną (17,1–33,4%), β-bisabololį (13,1–15,0%), β-kariofileną (6,2–9,8%) ir myrceną (6,1–6,7%). Kituose trijuose eteriniuose aliejuose kai kurie pagrindiniai komponentai yra skirtingi. Viename aliejuje vyravo α-humulenas (33,2%), β-kariofilenas (14,5%), α-zingiberenas (5,6%) ir myrcenas (5,1%), antrame – α-humulenas (14,2%), myrcenas (10,5%), β-farnesenas (9,5%) ir β-bisabalolas (9,6%), trečiame – γ-elemenas (14,0%), myrcenas (8,5%), β-farnesenas (7,8%) ir α-humulenas (6,6%). Dauguma komponentų (47,–73,5%) yra seskviterpeniniai angliavandeniliai. Monocikliniai seskviterpenoidai trijuose apynio pavyzdžiuose sudarė 47,2–59,8%, kituose dviejuose – 28,6–35,4%. Junginių su humulano, bisabolano, kariofilano, farnesano ir elemano anglies skeletais yra 57,6–70,8% anksčiau minėtuose trijuose eteriniuose aliejuose ir 42,7–53,6% kituose dviejuose. Identifikuoti 98 junginiai sudaro 86,1–98,8% eterinių aliejų.