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# Analysis and Sensory Evaluation of Jostaberry (*Ribes x nidigrolaria* Bauer) Volatiles

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**ABSTRACT:** Volatiles of jostaberries (*Ribes x nidigrolaria* Bauer)—a hybrid of black currant (*Ribes nigrum* L.) and gooseberry (*Ribes uva-crispa* L.)—were isolated via vacuum headspace extraction and analyzed by capillary gas chromatographic methods for the first time. (*E*)-Hex-2-enal, (*E*)-hex-2-en-1-ol, (*Z*)-hex-3-enal, (*Z*)-hex-3-en-1-ol, methyl butanoate, ethyl butanoate, 2-methylbut-3-en-2-ol, and 1,8-cineol turned out to be the most dominant volatiles. The variability of the volatile profile was shown by the analysis of jostaberries harvested from different locations in Southern Germany and in different years. In addition to ripe jostaberries, underripe berries were also investigated and changes in the volatile profile were followed during the ripening process. By using sensory analysis, key aroma compounds were elucidated. An aroma model prepared by mixing most odor active compounds ((*Z*)-hex-3-enal, 1,8-cineol, ethyl butanoate, (*E*)-hex-2-enal, (*E*)-hex-3-enal, hexanal, pent-1-en-3-one, methyl butanoate, ethyl hexanoate, and oct-1-en-3-one) in their naturally occurring concentrations showed an overall aroma very similar to that of fresh jostaberries.

KEYWORDS: Ribes x nidigrolaria Bauer, jostaberry, volatiles, aroma, reconstitution

#### ■ INTRODUCTION

Jostaberry (Ribes x nidigrolaria Bauer) is a hybrid of black currant (Ribes nigrum L.) and gooseberry (Ribes uva crispa L.). Both gooseberries and black currants suffered from American powdery mildew or rather leaf spot and white pine blister rust.<sup>1</sup> Therefore, the aim of the first hybridization experiments conducted already in 1929 was the creation of a new species of soft fruit, exhibiting higher resistance to yield- and quality-reducing diseases.<sup>1,2</sup> Jostaberries turned out to be extremely profitable in terms of yield and to exceed the vigor of the parent species. The plants are as hardy as those of gooseberries but have the benefit of having no thorns. At full ripeness, the fruits are dark colored and their size is between those of gooseberries and black currants.<sup>1</sup> Early jostaberry hybrids were not suitable for mechanical harvesting and the commercial production remained limited. Therefore, attempts have been made to breed varieties that can be harvested easily and mechanically.<sup>3</sup> Jostaberries are not only suitable for fresh consumption but also for the production of jams and beverages.<sup>4</sup> Official data on the cultivation of jostaberries are not available; obviously, they still represent a niche product.

Thus far, analytical investigations of jostaberries have been focused on ingredients exhibiting antioxidative properties. First studies date already from 1985; especially during the past decade, this aspect has been studied in depth.<sup>5–9</sup> The phenol content, the antioxidant activity and the concentrations of anthocyanins in jostaberries are between those of gooseberries and black currants. Major anthocyanins of jostaberries were reported to reflect those of both parent species.<sup>8</sup> Another benefit of jostaberries is the high vitamin C content, which reaches nearly the levels in black currants.<sup>1</sup>

Already in 1978 Bauer noted that jostberries combine both the aroma of gooseberries and the typical notes of black currants.<sup>1</sup> However, flavor compounds of jostaberries have not

been studied thus far. Therefore, the objectives of the present study were (i) to identify and to quantify volatile jostaberry constituents, (ii) to demonstrate the degree of variability in the volatile composition, and (iii) to assess the contributions of single compounds to the overall aroma by gas chromatographyolfactometry (GC-O).

#### MATERIALS AND METHODS

**Fruits.** Jostaberries (cultivars not known) were harvested (handpicked) at different locations in Southern Germany in three seasons. 2010: Freising (19 July); 2011: Oberrottweil (30 June), Lindau (3 July), Deutenkofen (4 July and 11 July), Hangenham (4 July), Freising (13 July); 2012: Deutenkofen (2 July (2 batches)), Freising (16 July). Except for one batch harvested in the underripe state (Deutenkofen on 2 July, 2012), all other fruits were picked at the ripe state. The degree of ripeness was evaluated according to color and firmness. Underripe jostaberries are very hard and their color ranges only from green to light-red, whereas ripe jostaberries are considerably softer and nearly black. Black currants analyzed in this study were purchased at a local market in Freising, Germany (20 June, 2011); they were declared to originate from Oberkirch, a location in Southern Germany. All berries were analyzed within two days after harvest and purchase, respectively. Until analysis, they were stored at 4 °C.

**Chemicals.** Authentic reference chemicals were purchased from commercial sources (Aldrich, Steinheim, Germany; Merck, Darmstadt, Germany) or provided by *Frey+Lau GmbH* (Henstedt-Ulzburg, Germany). Heptan-2-ol was purchased from Fluka (Steinheim, Germany), sodium sulfate from Merck (Darmstadt, Germany) and citric acid, hydrochloric acid and sodium hydroxide from Sigma-Aldrich (Steinheim, Germany). All chemicals used were of analytical grade. The solvents diethyl ether (Honeywell Burdick & Jackson, Seelze,

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Table 1. Volatile Compounds Isolated by Means of VHS from Ripe Jostaberries Harvested in 2011 at Three Locations in Southern Germany<sup>a</sup>

|                                       |                   | Lindau <sup>c</sup>        | Deutenkofen <sup>e</sup>         | Hangenham <sup>e</sup>         |                |
|---------------------------------------|-------------------|----------------------------|----------------------------------|--------------------------------|----------------|
| compounds                             | $\mathrm{RI}^{b}$ | $\left[\mu g/kg\right]^d$  | $\left[\mu g/kg\right]^d$        | $\left[\mu g/kg\right]^d$      | remark         |
| C <sub>6</sub> -components            |                   | 4.0.01                     | 4.0.01                           | 4.0 0.                         |                |
| (E)-hex-2-enal                        | 1211              | $6027 \pm 439$             | 5793 ± 857                       | $5176 \pm 507$                 | f,g,h          |
| ( <i>E</i> )-hex-2-en-1-ol            | 1406              | 1663 + 159                 | 1745 + 920                       | 1547 + 634                     | f.g.i          |
| (Z)-hex-3-enal                        | 1138              | $798 \pm 125$              | $2799 \pm 426$                   | $1454 \pm 916$                 | fai            |
| (7) has 3 on 1 ol                     | 1384              | $730 \pm 123$<br>712 ± 143 | $401 \pm 03$                     | $502 \pm 185$                  | j,g,.<br>fai   |
| (E) how 2 anal                        | 1122              | $712 \pm 143$              | $\frac{1}{275} \pm 80$           | $302 \pm 103$                  | J,g,i<br>f a i |
| (E)-nex-3-enai                        | 1133              | $104 \pm 48$               | $2/3 \pm 80$                     | $240 \pm 20$<br>140 ± 21       | J,g,i<br>f a i |
| haven 1 al*                           | 1075              | $170 \pm 52$ (a)           | $120 \pm 10$ (L)                 | $140 \pm 21$                   | J,g,i<br>f a i |
| (T) have 2 are 1 all                  | 1355              | $1/0 \pm 35$ (a)           | $48 \pm 18 (0)$                  | $110 \pm 47$ (a,b)             | J,g,i<br>      |
| (E)-nex-3-en-1-ol                     | 1304              | /8 ± /                     | $52 \pm 20$                      | $5/\pm 1/$                     | <i>J,1</i>     |
| (Z)-hex-2-enal                        | 1194              | $45 \pm 10$                | $66 \pm 25$                      | 39 ± 7                         | j,k            |
| (Z)-hex-2-en-1-ol                     | 1417              | $5 \pm 1$                  | $5 \pm 2$                        | $7 \pm 4$                      | f,i            |
| hex-5-enal**                          | 1127              | n.q.' (b)                  | $4 \pm 1$ (a)                    | $4 \pm 1$ (a)                  | j,k            |
| esters                                |                   |                            |                                  |                                | <i>c</i> .     |
| methyl butanoate**                    | 975               | $3664 \pm 905$ (b)         | $1851 \pm 448 (c)$               | $5409 \pm 621$ (a)             | f,g,i          |
| ethyl butanaote***                    | 1034              | $633 \pm 112$ (b)          | $445 \pm 86 (b)$                 | $1698 \pm 176$ (a)             | f,g,i          |
| methyl (E)-but-2-enoate*              | 1096              | $139 \pm 27$ (a)           | $92 \pm 16$ (b)                  | $108 \pm 6 (a,b)$              | f,g,i          |
| ethyl (E)-but-2-enoate***             | 1158              | $24 \pm 5$ (b)             | $24 \pm 4$ (b)                   | $77 \pm 9$ (a)                 | f,g,i          |
| methyl hexanaote***                   | 1184              | $63 \pm 4 (a)$             | $19 \pm 2$ (b)                   | $74 \pm 10$ (a)                | f,g,h          |
| methyl benzoate                       | 1613              | 48 ± 5                     | $62 \pm 5$                       | 48 ± 9                         | f,g,i          |
| ethyl hexanoate***                    | 1232              | $13 \pm 5 (a,b)$           | n.q. (b)                         | $26 \pm 8 (a)$                 | f,g,h          |
| ethyl benzoate                        | 1659              | $13 \pm 11$                | $22 \pm 1$                       | $24 \pm 4$                     | f,g,i          |
| hexyl acetate***                      | 1263              | $3 \pm 2$ (b)              | $4 \pm 1$ (b)                    | $23 \pm 5$ (a)                 | f,h            |
| methyl octanoate*                     | 1387              | $20 \pm 6 (a,b)$           | $11 \pm 2 (b)$                   | $23 \pm 0$ (a)                 | f,h            |
| benzyl acetate                        | 1725              | $9 \pm 1$                  | $10 \pm 4$                       | $14 \pm 4$                     | f,i            |
| butyl acetate*                        | 1061              | $5 \pm 1$ (b)              | $4 \pm 3$ (b)                    | $11 \pm 3$ (a)                 | f,i            |
| ethyl octanoate**                     | 1436              | $3 \pm 2$ (b)              | $2 \pm 2$ (b)                    | $11 \pm 2 (a)$                 | f,h            |
| (E)-hex-2-enyl acetate                | 1332              | $8 \pm 2$                  | $16 \pm 8$                       | 9 ± 4                          | f,i            |
| 2-methylbut-3-en-2-yl acetate         | 1251              | n.d. <sup>m</sup>          | $7 \pm 3$                        | 8 ± 3                          | f,k,i          |
| methyl salicylate                     | 1743              | $13 \pm 5$                 | $12 \pm 1$                       | $8 \pm 2$                      | f,h            |
| methyl decanoate***                   | 1588              | n.g. (b)                   | n.g. (b)                         | 6 + 2 (a)                      | f.h            |
| 2-methylpropyl acetate***             | 1005              | n.d. (b)                   | n.d. (b)                         | 5 + 1 (a)                      | f.n            |
| ethyl salicylate*                     | 1783              | n.q. (b)                   | $2 \pm 1$ (a,b)                  | $3 \pm 1$ (a)                  | f,i            |
| ethyl propanoate                      | 945               | n.q.                       | n.q.                             | n.q.                           | f,i            |
| 3-methylbutyl acetate                 | 1110              | n.d.                       | n.q.                             | n.q.                           | f,i            |
| octyl acetate                         | 1463              | n.d.                       | n.d.                             | n.q.                           | f,i            |
| chrysanthenyl acetate                 | 1802              | n.d.                       | n.q.                             | n.d.                           | j,k            |
| linalyl acetate                       | 1552              | n.q.                       | n.d.                             | n.q.                           | f,i            |
| ethyl decanoate                       | 1635              | n.q.                       | n.d.                             | n.q.                           | f,i            |
| alcohols                              |                   |                            |                                  |                                |                |
| 2-methylbut-3-en-2-ol**               | 1041              | $1182 \pm 197$ (b)         | $1051 \pm 287$ (b)               | $1995 \pm 144$ (a)             | f,g,i          |
| 2-methylpropan-1-ol**                 | 1084              | $33 \pm 7$ (b)             | $26 \pm 6 (b)$                   | $117 \pm 32$ (a)               | f,g,i          |
| (Z)-pent-2-en-1-ol                    | 1322              | $30 \pm 2$                 | $37 \pm 5$                       | $39 \pm 3$                     | f,i            |
| butan-1-ol**                          | 1142              | $15 \pm 2$ (b)             | $8 \pm 3$ (b)                    | $38 \pm 10$ (a)                | f,i            |
| (R)-oct-1-en-3-ol***                  | 1452              | $35 \pm 9$ (b)             | $134 \pm 27$ (a)                 | $25 \pm 4$ (b)                 | f,g,i,o        |
| pent-1-en-3-ol                        | 1160              | $24 \pm 3$                 | $23 \pm 3$                       | $24 \pm 3$                     | f,h            |
| octan-1-ol $(7)$ 1 $25$ 1 1 1**       | 1560              | $9 \pm 4$                  | $12 \pm 3$                       | $14 \pm 2$                     | f,h            |
| (Z)-nexa-3,5-dien-1-ol <sup>***</sup> | 1507              | $12 \pm 3$ (a)             | n.d. (b) $(-1)$                  | $10 \pm 2$ (a)                 | j,ĸ<br>        |
| pental-1-of**                         | 1232              | 1.q.(b)                    | $0 \pm 1$ (a)<br>$5 \pm 0$ (ab)  | $9 \pm 2$ (a)<br>$7 \pm 1$ (a) | ],1<br>f;      |
| (E) pent 2 en 1 ol**                  | 13/1              | $4 \pm 1 (0)$              | $3 \pm 0 (a, b)$                 | $7 \pm 1$ (a)<br>$7 \pm 1$ (b) | ј,1<br>ј. ћ    |
| ethanol**                             | 031               | 7 + 2 (3)                  | $10 \pm 0$ (a)<br>$12 \pm 5$ (a) | $r \pm r(0)$<br>nd (b)         | j,∼<br>fi      |
| pentan-2-ol                           | 1123              | 3 + 3                      | n.a.                             | 3 + 3                          | j,.<br>f.i     |
| nonan-1-ol                            | 1646              | n.g.                       | <br>n.g.                         | <u> </u>                       | ,;.<br>f,i     |
| 2-ethylhexan-1-ol                     | 1492              | n.d.                       | n.q.                             | n.q.                           | f,i            |
| 2-phenylethan-1-ol                    | 1906              | n.d.                       | n.q.                             | n.q.                           | f,i            |
| ( <i>E</i> )-hexa-3,5-dien-1-ol       | 1504              | n.q.                       | n.d.                             | n.d.                           | j,k            |

#### Table 1. continued

| compounds         R4" $[\mu g/kg]^d$ $[\mu g/kg]^d$ $[\mu g/kg]^d$ remark           terpment/terpene alcohols         1,3-cincel         1200         647 ± 115         536 ± 50         557 ± 84 $f_g h$ terpinent-alcohols         1685         26 ± 12         22 ± 3         15 ± 3 $f_g h p$ a'terpinend         1685         26 ± 12         22 ± 3         15 ± 3 $f_g h p$ 2-hydrogy-1,8-cincel**         1721         3 ± 1 (b)         4 ± 0 (a)         4 ± 1 $f_h$ 2-hydrogy-1,8-cincel**         1721         3 ± 1 (b)         4 ± 0 (a)         2 ± 2 (a,b) $f_h$ 2-hydrogy-1,8-cincel**         1272         n.4. (b)         13 ± 2 (a)         n.4. (b) $f_{h} d$ 2-hydrogy-1,8-cincel**         1272         n.4. (b)         3 ± 2 (a,b)         n.4. (b) $f_{h} d$ 2-hydrogy-1,8-cincel**         1252         n.4. (b)         3 ± 1 (a)         n.4. (b) $f_{h} d$ 2-hydrogy-1,8-cincel**         1255         n.4. (b)         3 ± 0 (a)         n.4. (b) $f_{h} d$ 2-hydrogy-1,8-cincel**         1255         n.4. (b)         3 ± 0 (a)         n.4. (b) $f_{h} d$  |                                   |                   | Lindau <sup>c</sup> | Deutenkofen <sup>e</sup> | Hangenham <sup>e</sup> |         |
|--|-----------------------------------|-------------------|---------------------|--------------------------|------------------------|---------|
| treprises/tr | compounds                         | $\mathrm{RI}^{b}$ | $[\mu g/kg]^d$      | $[\mu g/kg]^d$           | $[\mu g/kg]^d$         | remark  |
| 1.8-(nol)1200 $647 \pm 115$ $536 \pm 50$ $557 \pm 84$ $fgh$ terpinen-4-0 <sup>th</sup> 1592 $101 \pm 39(a)$ $47 \pm 6(ab)$ $34 \pm 4(b)$ $fgi$ a-terpineol1685 $26 \pm 12$ $22 \pm 3$ $15 \pm 3$ $fghq$ $\beta$ -pinen1093 $6 \pm 3$ $7 \pm 2$ $8 \pm 2$ $fh$ $2$ -hydroxy-1.8-cincol <sup>±±</sup> 1721 $3 \pm 1(b)$ $4 \pm 0(a)$ $4 \pm 1(a)$ $f_{4}q$ $\gamma$ -terpinene1238 $4 \pm 2$ $6 \pm 1$ $4 \pm 1$ $ji$ $sabinene±a$ 1106 $n.d.(b)$ $4 \pm 1(a)$ $2 \pm 2(ab)$ $n,d.(b)$ $fgi$ $fgi$ $ggi$ $fgi$ $ggi$ $fgi$ $2hydroxy-1.8-cincol±$ 1196 $n.q.(b)$ $3 \pm 1(a)$ $n.d.(b)$ $fgi$ prencha-1.4-dien-7-ol <sup>±±±</sup> 1255 $n.d.(b)$ $3 \pm 0(a)$ $n.d.(b)$ $fgi$ prencha-1.4-dien-7-ol <sup>±±±</sup> 1255 $n.d.(b)$ $3 \pm 0(a)$ $n.q.(b)$ $fgi$ arpinene1051 $n.d.$ $n.d.$ $n.q.$ $n.q.$ $fgi$ arpinene1165 $n.d.$ $n.d.$ $n.d.$ $n.q.$ $fgi$ morenel1666 $n.q.$ $n.d.$ $n.d.$ $fgi$ nonal <sup>±±</sup> 1391 $n.d.(b)$ $9 \pm 3(a)$ $5 \pm 0(a)$ $fji$ prop 2-enal <sup>±±</sup> 1391 $n.q.(b)$ $9 \pm 3(a)$ $5 \pm 0(a)$ $fji$ prop 2-enal <sup>±±</sup> 1391 $n.q.(b)$ $9 \pm 3(a)$ $a.d.(b)$ $fji$ prop 2-enal <sup>±±</sup> 1391 $n.d.(b)$ $9 \pm 3(a)$ $a.d.(b)$ $f$   | terpenes/terpene alcohols         |                   |                     |                          |                        |         |
| terpinen-4-0 <sup>*</sup> 1592         101 ± 39 (a)         47 ± 6 (ab)         34 ± 4 (b)         fg/ $a$ -terpined         1685 $26 \pm 12$ $22 \pm 3$ $15 \pm 3$ $fg/apa$ $\beta$ -pinene         1093 $6 \pm 3$ $7 \pm 2$ $8 \pm 2$ $fh$ $2hydroxy-Ly-cincel**$ 1721 $3 \pm 1$ (b) $4 \pm 0$ (a) $4 \pm 1$ $fi$ $2hydroxy-Ly-cincel**$ 1106 $n.d$ (b) $4 \pm 1$ (a) $2 \pm 2$ ( $a,b$ ) $n_4$ (b) $fgi$ $2hydroxy-Ly-cincel**$ 1272 $n.q$ (b) $3 \pm 1$ (a) $n.q$ (b) $fgi$ $p$ -menth- $1.4$ -dien-7-ol***         1255 $n.d$ (b) $3 \pm 1$ (a) $n.d$ (b) $fgi$ $p$ -menth**         1255 $n.d$ (b) $3 \pm 0$ (a) $n.d$ (b) $fgi$ $p$ -remer**         1255 $n.d$ (b) $3 \pm 0$ (a) $n.d$ (b) $fgi$ $p$ -remer**         103 $n.d$ $n.d$ $n.d$ (b) $fgi$ $p$ -remer**         103 $n.d$ $n.d$ $n.d$ (b) $fgi$ $p$ -remer**  | 1,8-cineol                        | 1200              | 647 ± 115           | $536 \pm 50$             | 557 ± 84               | f,g,h   |
| $a$ terminel         1685 $26 \pm 12$ $22 \pm 3$ $15 \pm 3$ $fghp$ $\beta$ -pinene         1093 $6 \pm 3$ $7 \pm 2$ $8 \pm 2$ $fh$ $2$ -hydroxy, 1,2-cneol**         1238 $4 \pm 2$ $6 \pm 1$ $4 \pm 1$ $fi$ $x$ -trepinene         1238 $4 \pm 2$ $6 \pm 1$ $4 \pm 1$ $fi$ $x$ -hydroxy, 1,8-cneol*         1859 $4 \pm 0$ $0$ $2 \pm 2$ ( $_{3}$ b) $n_{4}$ $b$ $f_{4}$ d $2$ -hydroxy, 1,8-cneol*         1859 $4 \pm 0$ $0$ $2 \pm 2$ ( $_{3}$ b) $n_{4}$ $b$ $f_{6}$ d           terpinolene***         1196 $n_{4}$ (b) $3 \pm 2$ ( $_{3}$ ) $n_{4}$ $n_{4}$ $n_{4}$ $n_{4}$ $h$ $h$ $p$ -menth= $1,4$ -dien 7-ol***         2053 $n_{4}$ (b) $3 \pm 0$ ( $a$ ) $n_{4}$ (b) $fgi$ $p$ -menth= $1,4$ -dien 7-ol***         2053 $n_{4}$ (b) $3 \pm 0$ ( $a$ ) $n_{4}$ (b) $fgi$ $p$ -groment***         1051 $n_{4}$ $n_{4}$ $n_{4}$ $n_{4}$ $fgi$  | terpinen-4-ol*                    | 1592              | $101 \pm 39$ (a)    | 47 ± 6 (a,b)             | $34 \pm 4 (b)$         | f,g,i   |
| $\beta$ -pince193 $6 \pm 3$ $7 \pm 2$ $8 \pm 2$ $fh$ $2$ hydroxy 1,8-cheol**1721 $3 \pm 1$ (b) $4 \pm 0$ (a) $4 \pm 1$ (a) $fk_d$ $\gamma$ -terpinene1238 $4 \pm 2$ $6 \pm 1$ $4 \pm 1$ $fi$ $shinene**$ 1106 $nd$ (b) $4 \pm 1$ (a) $2 \pm 2$ (a,b) $fi$ $2$ hydroxy 1,8-cheol*1859 $4 \pm 0$ (a) $2 \pm 2$ (a,b) $nq$ (b) $fgi$ $2$ hydroxy 1,8-cheol*1272 $nq$ (b) $3 \pm 1$ (a) $nq$ (b) $fgi$ $p$ -menth-1,4-dien-7-ol***1272 $nq$ (b) $3 \pm 1$ (a) $nd$ (b) $fgi$ $p$ -menth-1,4-dien-7-ol***1255 $nd$ (b) $3 \pm 0$ (a) $nd$ (b) $fgi$ $p$ -menth-1,4-dien-7-ol***1255 $nd$ (b) $3 \pm 0$ (a) $nd$ (b) $fgi$ $p$ -menth-1,4-dien-7-ol***1255 $nd$ (b) $3 \pm 0$ (a) $nd$ (b) $fgi$ $p$ -remer**1051 $nq$ $nq$ $nq$ $nq$ $fgi$ $amphene1051ndndndnqfgimenthol1644ndnqnqnqfgiamphor1499ndndnqnqfgiaddhydsfinqnqnqnqfgimonanal**1391nq (b)9 \pm 3 (a)5 \pm 0 (a)ffip-co-2-mal1660nqndndfgiacbnyhordshyde1516nqnqnqnd$   | $\alpha$ -terpineol               | 1685              | $26 \pm 12$         | $22 \pm 3$               | $15 \pm 3$             | f,g,h,p |
| 2-hydroxy-1.8-cincel**       1721 $3 \pm 1$ (b) $4 \pm 0$ (a) $4 \pm 1$ (a) $fkq$ $\gamma$ terpinene       1238 $4 \pm 2$ $6 \pm 1$ $4 \pm 1$ (a) $fkq$ $z$ sbinene**       1106       n.d. (b) $4 \pm 1$ (a) $2 \pm 2$ (ab) $n.q.$ (b) $fkq$ $2$ -hydroxy-1.8-cincel*       1859 $4 \pm 0$ (a) $2 \pm 2$ (ab) $n.q.$ (b) $fkq$ $2$ -hydroxy-1.8-cincel**       1272 $n.q.$ (b) $3 \pm 1$ (a) $n.q.$ (b) $fkq$ immene***       1196 $n.q.$ (b) $3 \pm 0$ (a) $n.d.$ (b) $fkq$ $p$ -enthal.4-dien.7-ol***       2053 $n.d.$ (b) $3 \pm 0$ (a) $n.d.$ (b) $fk$ $p$ -cymene***       1255 $n.d.$ (b) $3 \pm 0$ (a) $n.q.$ (b) $fk$ $p$ -cymene***       1051 $n.q.$ $n.q.$ $n.q.$ $fkq$ myrcene       1165 $n.d.$ $n.q.$ $n.q.$ $fkq$ membol       1644 $n.d.$ $n.q.$ $n.q.$ $fkq$ camphor       1499 $n.d.$ $n.d.$ $n.q.$ $fk$ prop2-enal**<   | $\beta$ -pinene                   | 1093              | 6 ± 3               | $7 \pm 2$                | $8 \pm 2$              | f,h     |
| $\gamma$ -terpinene12384 ± 26 ± 14 ± 1 (a)2 ± 2 (ab) $fi$ sabinene**1106n.d. (b)4 ± 1 (a)2 ± 2 (ab) $fi$ 2-hydroxy-1.8-cincel*18594 ± 0 (a)2 ± 2 (ab) $n.q. (b)$ $fkq$ terpinolene***1272 $n.q. (b)$ $13 \pm 2 (a)$ $n.q. (b)$ $fgi$ p-mentha-1.4-dien-7-ol***2053 $n.d. (b)$ $3 \pm 0 (a)$ $n.d. (b)$ $fgi$ p-cymene***1255 $n.d. (b)$ $3 \pm 0 (a)$ $n.q. (b)$ $fgi$ camphene1013 $n.d.$ $n.q.$ $n.q.$ $fgi$ myrcene1165 $n.d.$ $n.d.$ $n.q.$ $fgi$ myrcene1166 $n.q.$ $n.d.$ $n.q.$ $fgi$ menthol1644 $n.d.$ $n.q.$ $n.q.$ $fj$ addydyds $(f)$ $fgi$ $fji$ $(f)$ -pert-2-enal112022 ± 4 $3 6 \pm 10$ $25 \pm 4$ $fji$ nonanal**1391 $n.q.$ $n.q.$ $n.q.$ $fji$ proponal**801 $n.q.$ $n.q.$ $n.q.$ $fji$ bernsdelende1516 $n.q.$ $n.q.$ $n.q.$ $fji$ $(f,f_i)$ -hept-2-enal1516 $n.q.$ $n.q.$ $n.d.$ $fji$ proponal**1309 $n.q.$ $n.q.$ $n.d.$ $fji$ $(f)$ -bept-2-enal1516 $n.q.$ $n.q.$ $n.d.$ $fji$ $(f,f_i)$ -hept-2-enal1516 $n.q.$ $n.q.$ $n.d.$ $fji$ $(f,f_i)$ -   | 2-hydroxy-1,8-cineol**            | 1721              | $3 \pm 1$ (b)       | $4 \pm 0$ (a)            | $4 \pm 1$ (a)          | f,k,q   |
| shince**         1106         nd. (b) $4 \pm 1$ (a) $2 \pm 2$ (ab) $fi$ $2hydroxy-1,8 cincel^{2}$ 1859 $4 \pm 0$ (a) $2 \pm 2$ (ab)         nq. (b) $fkq$ terpinoleme***         1196         n.q. (b) $3 \pm 1$ (a)         nd. (b) $fgi$ imonene**         1196         n.q. (b) $3 \pm 0$ (a)         nd. (b) $fk$ $p$ -cymene***         1255         nd. (b) $3 \pm 0$ (a)         nd. (b) $fk$ $p$ -cymene***         1051         n.q.         n.q.         n.q. $fj$ camphene         1013         n.d.         n.q.         n.q. $fj$ menthol         1644         n.d.         n.q.         n.q. $fj$ camphor         1499         n.d.         n.d.         n.d. $fj$ diddhyds           25 ± 4 $fj$ $fj$ romanal**         1391         n.q. (b)         9 ± 3 (a) $5 \pm 0$ (a) $fj$ prop2-canal**         1391         n.q. (b) $7 \pm 3$ (a)         n.d. (b) $fj$ nonana**   | γ-terpinene                       | 1238              | $4 \pm 2$           | $6 \pm 1$                | $4 \pm 1$              | f,i     |
| 2-bydroxy-1.8-cincel*       1859 $4 \pm 0$ (a) $2 \pm 2$ (ab) $n.q.$ (b) $jk.q$ terpinolene***       172 $n.q.$ (b) $3 \pm 1$ (a) $n.q.$ (b) $jk.q$ imonene**       1196 $n.q.$ (b) $3 \pm 1$ (a) $n.q.$ (b) $jk.q$ p-entha-1,4-dien-7-ol***       2053 $n.d.$ (b) $3 \pm 0$ (a) $n.q.$ (b) $jk$ p-eymene***       1255 $n.d.$ (b) $3 \pm 0$ (a) $n.q.$ (b) $jk$ a-pinene       1013 $n.d.$ $n.q.$ $n.q.$ $jk$ a-pinene       1013 $n.d.$ $n.q.$ $n.q.$ $jkj$ camptor       1499 $n.d.$ $n.q.$ $n.q.$ $jkj$ camptor       1499 $n.d.$ $n.d.$ $n.q.$ $jk$ camptor       1499 $n.d.$ $n.d.$ $n.d.$ $jk$ borneol       1686 $n.q.$ $n.d.$ $n.d.$ $jk$ prop2-zenal**       1391 $n.q.$ (b) $9 \pm 3$ (a) $5 \pm 0$ (a) $jh$ propal**       801 $n.q.$ (b) $2 \pm 4$ (a) $a.$   | sabinene**                        | 1106              | n.d. (b)            | $4 \pm 1$ (a)            | $2 \pm 2 (a,b)$        | f,i     |
| terpinolene***1272n.q. (b) $13 \pm 2$ (a)n.q. (b) $fgi$ limonere**1196n.q. (b) $3 \pm 1$ (a)n.d. (b) $fgi$ p-menth-1,4.dien-7-ol***2053n.d. (b) $3 \pm 0$ (a)n.q. (b) $fi$ p-cymene***1255n.d. (b) $3 \pm 0$ (a)n.q. (b) $fj$ camphene1051n.q.n.q.n.q.n.q. $fgi$ myrcene1165n.d.n.d.n.q.n.q. $fgi$ menthol1644n.d.n.q.n.q. $fj$ camphor1499n.d.n.d.n.d. $n.d.$ $fj$ addhyds $fj$ $fj$ cambor1686n.q.n.d.n.d. $fj$ nonanl**1391n.q. (b) $9 \pm 3$ (a) $5 \pm 0$ (a) $fj$ prop-2-enal**843n.q. (b) $14 \pm 7$ (a)n.d. (b) $fj$ prop-anl**801n.q.n.q.n.q. $fj$ benzidehyde1516n.q.n.q.n.q. $fj$ 2-methylbutanal909n.q.n.d.n.d. $fj$ 2-methylbutanal912n.q.n.d. $n.q.fj3-methylbutanal912n.q.n.d.n.q.fj2-methylbutanal912n.q.fjfj3-methylbutanal912n.q.fjfj3-methylbutanal912n.d.fjfj2-methylbutanal912n.d.$   | 2-hydroxy-1,8-cineol*             | 1859              | $4 \pm 0$ (a)       | $2 \pm 2$ (a,b)          | n.q. (b)               | f,k,q   |
|  | terpinolene***                    | 1272              | n.q. (b)            | $13 \pm 2 (a)$           | n.q. (b)               | f,g,i   |
| p-mentha-1,4-dien-7-ol***2053n.d. (b) $3 \pm 0$ (a)n.d. (b) $jk$ p-cymene***1255n.d. (b) $3 \pm 0$ (a)n.q. (b) $ji$ camphene1051n.q.n.q.n.q. $fi$ $arpinene$ 1013n.d.n.q.n.q. $fgi$ myrcene1165n.d.n.q.n.q. $fgi$ menthol1644n.d.n.q.n.q. $fgi$ camphor1499n.d.n.d.n.d.n.d.borneol1686n.q.n.d.n.d. $fj$ alddhyds $(b)$ $2 \pm 4$ $36 \pm 10$ $2 \pm 4$ $fj$ nonanl**1120 $22 \pm 4$ $36 \pm 10$ $5 \pm 0$ (a) $fj$ prop-2-enal**843n.q. (b) $9 \pm 3$ (a) $5 \pm 0$ (a) $fj$ prop-2-enal**801n.q. (b) $7 \pm 3$ (a)n.d. (b) $fj$ prop-2-enal**801n.q.n.q. $n.q.$ $fj$ prop-2-enal**1216n.q.n.d. $fj$ $fj$ prop-2-enal**801n.q. $n.q.$ $n.q.$ $fj$ prop-2-enal**1210 $n.q.$ $n.d.$ $fj$ $fj$ prop-2-enal**801n.q. $fj$ $fj$ prop-2-enal**1217n.d. $n.q.$ $n.d.$ $fj$ prop-2-enal**1217 $n.d.$ $n.q.$ $fj$ prop-2-enal**1209 $n.q.$ $n.d.$ $fj$ prop-2-enal**1217 $n.d.$ $n.d.$ <td>limonene**</td> <td>1196</td> <td>n.q.(b)</td> <td><math>3 \pm 1</math> (a)</td> <td>n.d. (b)</td> <td>f,g,i</td>  | limonene**                        | 1196              | n.q.(b)             | $3 \pm 1$ (a)            | n.d. (b)               | f,g,i   |
| $p$ -cymene***1255n.d.(b) $3 \pm 0$ (a)n.q. (b) $fi$ camphene1051n.q.n.q.n.q. $fgi$ $ar$ pinene1013n.d.n.q.n.q. $fgi$ myrcene1165n.d.n.d.n.q. $fgi$ menthol1644n.d.n.q.n.q. $fgi$ camphor1499n.d.n.d.n.q. $fgi$ borneol1686n.q.n.d.n.d. $n.d.$ $fgi$ $alddhyds$ $fgi$ $fgi$ $fgi$ (E)-pent-2-enal112022 $\pm 4$ $36 \pm 10$ $25 \pm 4$ $fgi$ $prop-2-enal**843n.q. (b)9 \pm 3 (a)5 \pm 0 (a)ffiprop-2-enal**843n.q. (b)7 \pm 3 (a)n.d. (b)fgiprop-3-enal**801n.q. (b)7 \pm 3 (a)n.d. (b)fgiprop-3-enal**801n.q. (b)7 \pm 3 (a)n.d. (b)fgiprop-3-enal**1516n.q.n.q.n.d.fgiberzaldehyde1516n.q.n.d.n.d.fgi(E,E)-hept-2,4-dienal1475n.d.n.q.n.d.fgia-methylbutanal909n.q.n.d.n.d.fgia-to-sone**100920 \pm 4 (b)62 \pm 6 (a)49 \pm 9 (a)ffhacetophenone1254n.d.n.q.n.d.fgiacetophenone1264n.d.n.q.fgi$   | <i>p</i> -mentha-1,4-dien-7-ol*** | 2053              | n.d. (b)            | $3 \pm 0 (a)$            | n.d. (b)               | j,k     |
| camphene1051n.q.n.q.n.q.n.q.n.q. $fi$ $ar$ -pinene1013n.d.n.q.n.q. $n.q.$ $fgi$ myrcene1165n.d.n.d.n.q. $n.q.$ $fgi$ menthol1644n.d.n.q.n.q. $fgi$ camphor1499n.d.n.d.n.q. $fgi$ borneol1686n.q.n.d.n.d. $fgi$ <i>alddhydes</i> $fgi$ $fgi$ <i>alddhydes</i> $fgi$ $fgi$ <i>aldehydes</i> $fgi$ $fgi$ nonanal**1391n.q. (b) $9 \pm 3$ (a) $5 \pm 0$ (a) $fgi$ prop-2-enal**843n.q. (b) $7 \pm 3$ (a)n.d. (b) $fgi$ benzaldehyde1516n.q. $n.q.$ $n.q.$ $fgi$ 2-methylbutanal909n.q. $n.d.$ $n.d.$ $fgi$ 3-methylbutanal912n.q. $n.d.$ $n.d.$ $fgi$ $(E,E)-hept-2-enal137n.d.n.q.n.d.fgidetoriesfgifgifgifgidetoriesfgifgifgifgidetoriesfgi<$   | <i>p</i> -cymene***               | 1255              | n.d.(b)             | $3 \pm 0 (a)$            | n.q. (b)               | f,i     |
| $a$ -pinene1013n.d.n.q.n.q. $fgi$ myrcene1165n.d.n.d.n.q. $fgi$ menthol1644n.d.n.q.n.q. $fj$ camphor1499n.d.n.d.n.q. $fj$ borneol1686n.q.n.d.n.d. $n.d.$ $fj$ aldehyds $fj$ $fj$ $fj$ $fj$ $fj$ annonanl**112022 ± 4 $36 \pm 10$ $25 \pm 4$ $fj$ prop-2-enal**843n.q. (b) $9 \pm 3$ (a) $5 \pm 0$ (a) $fj$ propanal**801n.q. (b) $7 \pm 3$ (a)n.d. (b) $fj$ propanal**801n.q.n.q. $n.q.$ $fj$ beraddehyde1516n.q. $n.q.$ $n.q.$ $fj$ $(E,E)$ -hept-2,4-dienal1475n.d. $n.q.$ $n.d.$ $fj$ $2$ -methylbutanal909 $n.q.$ $n.d.$ $n.d.$ $fj$ $3$ -methylbutanal912 $n.q.$ $n.d.$ $n.d.$ $fj$ $i$ -to-s-one**1009 $20 \pm 4$ (b) $62 \pm 6$ (a) $49 \pm 9$ (a) $fj$ $octan-3-one$ 1254 $n.q.$ $n.q.$ $n.q.$ $fj$ $i$ -to-s-one**1009 $20 \pm 4$ (b) $62 \pm 6$ (a) $49 \pm 9$ (a) $fj$ $i$ -to-s-one1460 $n.d.$ $n.q.$ $n.q.$ $fj$ $i$ -to-s-one1596 $n.d.$ $n.q.$ $i$ $fj$ $i$ -to-s-one1596 $n.d.$ $n.q.$ $i$ $fj$ <td>camphene</td> <td>1051</td> <td>n.q.</td> <td>n.q.</td> <td>n.q.</td> <td>f,i</td>   | camphene                          | 1051              | n.q.                | n.q.                     | n.q.                   | f,i     |
| myrcene1165n.d.n.d.n.q. $n.q.$ $f.g.i$ methol1644n.d.n.q.n.q. $f.i$ camphor1499n.d.n.d.n.d. $f.i$ borneol1686n.q.n.d.n.d. $f.i$ aldehyds $f.i$ (E)-pent-2-enal1120 $22 \pm 4$ $36 \pm 10$ $25 \pm 4$ $f.i$ nonanal**1391n.q. (b) $9 \pm 3$ (a) $5 \pm 0$ (a) $f.i$ propanal**843n.q. (b) $14 \pm 7$ (a)n.d. (b) $f.i$ propanal**801n.q. (b) $7 \pm 3$ (a)n.d. (b) $f.i$ propanal**801n.q. (b) $7 \pm 3$ (a)n.d. (b) $f.i$ propanal**801n.q. (b) $7 \pm 3$ (a)n.d. (b) $f.i$ jendehyde1516n.q.n.q.n.q. $f.i$ $(E,E)$ -hepta-2,4-dienal1475n.d.n.d.n.d. $f.i$ 3-methylbutanal909n.q.n.d. $n.d.$ $f.i$ 3-methylbutanal912n.q.n.d. $f.i$ $f.i$ $(E)$ -hept-2-enal1317n.d. $n.q.$ $a.d.$ $f.j$ $actophenone$ 1254n.q. $2 \pm 2$ $2 \pm 2$ $f.j$ $(E)$ -hept-3-one1256n.d.n.q. $n.d.$ $f.j$ $(E)$ -henone1457n.d.n.d. $n.d.$ $f.j$ $(E)$ -geranylacetone1859n.q. $n.d.$ $n.d.$ $f.j$   | $\alpha$ -pinene                  | 1013              | n.d.                | n.q.                     | n.q.                   | f,g,i   |
| menthol1644n.d.n.q.n.q. $n.q.$ $f_i$ camphor1499n.d.n.d.n.q. $n.q.$ $f_i$ borneol1686n.q.n.d.n.d.n.d. $n.d.$ $f_i$ aldelydes $f_i$ $f_i$ $f_i$ $f_i$ (E)-pent-2-enal1120 $22 \pm 4$ $36 \pm 10$ $25 \pm 4$ $f_i$ propanal**1391n.q. (b) $9 \pm 3$ (a) $5 \pm 0$ (a) $f_i$ propanal**801n.q. (b) $14 \pm 7$ (a)n.d. (b) $f_i$ propanal**801n.q. $7 \pm 3$ (a)n.d. (b) $f_i$ benzaldehyde1516n.q.n.q.n.q. $f_i$ 2-methylbutanal909n.q.n.q.n.q. $f_i$ 3-methylbutanal912n.q.n.d.n.d. $f_i$ 3-methylbutanal912n.q.n.d.n.d. $f_i$ $ktoms$ $f_i$ $f_i$ $f_i$ $f_i$ $ctan-3-one **$ 1009 $20 \pm 4$ (b) $62 \pm 6$ (a) $49 \pm 9$ (a) $f_i$ octan-3-one1254n.q. $2 \pm 2$ $2 \pm 2$ $f_i$ acetophenone1640n.d.n.q. $n.q.$ $f_i$ oct-1-en-3-one1296n.d. $n.d.$ $n.d.$ $f_i$ $i_i$  | myrcene                           | 1165              | n.d.                | n.d.                     | n.q.                   | f,g,i   |
| camphor1499n.d.n.d.n.q. $n.q.$ $fi$ borneol1686n.q.n.d.n.d. $n.d.$ $n.d.$ $fi$ aldehydes22 ± 4 $3 6 \pm 10$ $25 \pm 4$ $fi$ nonanal**1391n.q. (b) $9 \pm 3$ (a) $5 \pm 0$ (a) $fh$ prop-2-enal**843n.q. (b) $14 \pm 7$ (a)n.d. (b) $fi$ propanal**801n.q. (b) $7 \pm 3$ (a)n.d. (b) $fi$ benzaldehyde1516n.q.n.q.n.q. $fi$ 2-methylbutanal909n.q.n.d.n.d. $fi$ 3-methylbutanal912n.q.n.d.n.d. $fi$ $i E(E)$ -hept-2-enal1317n.d.n.q.n.d. $fgi$ $k tornes$ $i = 10^{-1} - n \cdot 3 - 0ne^{**}$ 1009 $20 \pm 4$ (b) $62 \pm 6$ (a) $49 \pm 9$ (a) $fh$ octan-3-one1254n.q. $n.d.$ n.q. $fgi$ actorblenone1640n.d.n.q.n.d. $fgi$ $nethone$ 1457n.d.n.d. $n.q.$ $fgi$ $i forsi1296n.d.n.d.n.d.fgii forsi1296n.d.n.d.n.d.fgii forsi1296n.d.n.d.n.d.n.d.fgii forsi1296n.d.n.d.n.d.n.d.fgii forsi1296n.d.n.d.n.d.n.d.fgii forsi$   | menthol                           | 1644              | n.d.                | n.q.                     | n.q.                   | f,i     |
| borneol1686n.q.n.d.n.d.n.d. $fi$ addehydes(E)-pent-2-enal112022 ± 4 $36 \pm 10$ $25 \pm 4$ $f_i$ nonanl**1391n.q. (b) $9 \pm 3$ (a) $5 \pm 0$ (a) $f_i$ prop-2-enal**843n.q. (b) $14 \pm 7$ (a)n.d. (b) $f_i$ propanal**801n.q. (b) $7 \pm 3$ (a)n.d. (b) $f_i$ benzaldehyde1516n.q.n.q.n.q. $n.q.$ $n.q.$ (E,E)-hept-2,4-dienal1475n.d.n.q.n.q. $n.q.$ $f_i$ 2-methylbutanal909n.q.n.d. $n.d.$ $f_i$ 3-methylbutanal912n.q.n.d. $n.d.$ $f_i$ 61317n.d.n.q. $n.d.$ $f_i$ ctan-3-one1009 $20 \pm 4$ (b) $62 \pm 6$ (a) $49 \pm 9$ (a) $f_i$ octan-3-one1254n.q. $2.4 \pm 2$ $2 \pm 2$ $f_i$ acetophenone1640n.d.n.q. $n.q.$ $f_i$ oct-1-en-3-one1296n.d.n.d. $n.q.$ $f_i$ id/2-geranylacetone1859n.q.n.d. $n.d.$ $f_i$ othersCS-compounds963 $32 \pm 4$ $27 \pm 10$ $36 \pm 6$ $f_k k,r$ isoeugenol2315 $4 \pm 4$ n.d.n.d. $n.d.$ $f_i$ isoeugenol2315 $4 \pm 4$ n.d. $n.d.$ $n.d.$ $f_i$   | camphor                           | 1499              | n.d.                | n.d.                     | n.q.                   | f,i     |
| aldchydes(E)-pent-2-enal1120 $22 \pm 4$ $36 \pm 10$ $25 \pm 4$ $fi$ nonanal**1391n.q. (b) $9 \pm 3$ (a) $5 \pm 0$ (a) $fh$ prop-2-enal** $843$ n.q. (b) $14 \pm 7$ (a)n.d. (b) $fi$ propanal** $801$ n.q. (b) $7 \pm 3$ (a)n.d. (b) $fi$ benzaldehyde1516n.q.n.q.n.q. $n.q.$ benzaldehyde1516n.q.n.q.n.q. $fi$ 2-methylbutanal909n.q.n.d.n.d. $fi$ 3-methylbutanal912n.q.n.d.n.d. $fg,i$ benzaldehyde1317n.d.n.q.n.d. $fg,i$ ctones $i$ $i$ $i$ $i$ $i$ $i$ 2-methylbutanal912n.q.n.d. $n.d.$ $fg,i$ 3-methylbutanal912n.q. $i$ $i$ $i$ $(E)-hept-2-enaliiiiig,iiiiiiig,iiiiiiig,iiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiii$  | borneol                           | 1686              | n.q.                | n.d.                     | n.d.                   | f,i     |
| $(E)$ -pent-2-enal1120 $22 \pm 4$ $36 \pm 10$ $25 \pm 4$ $fi$ nonanal**1391n.q. (b) $9 \pm 3$ (a) $5 \pm 0$ (a) $fh$ prop-2-enal**843n.q. (b) $14 \pm 7$ (a)n.d. (b) $fi$ propanal**801n.q. (b) $7 \pm 3$ (a)n.d. (b) $fi$ benzaldehyde1516n.q. (b) $7 \pm 3$ (a)n.d. (b) $fi$ benzaldehyde1516n.q. (a,n.q.n.q. $fi$ 2-methylbutanal909n.q.n.d.n.d. $fi$ 3-methylbutanal912n.q.n.d.n.d. $fgi$ $(E)$ -hept-2-enal1317n.d.n.q.n.d. $fgi$ $ketones$ $gei$ $20 \pm 4$ (b) $62 \pm 6$ (a) $49 \pm 9$ (a) $f_i$ octan-3-one1254n.q. $2 \pm 2$ $2 \pm 2$ $f_i$ $gi$ $n.d.$ $n.d.$ $n.d.$ $f_i$ octan-3-one1254n.d. $n.d.$ $n.d.$ $f_i$ $(Z)$ -geranylacetone1640 $n.d.$ $n.d.$ $n.d.$ $f_i$ $(Z)$ -geranylacetone1859 $n.g.$ $n.d.$ $n.d.$ $n.d.$ $f_i$ $(Z)$ -geranylacetone2053 $32 \pm 4$ $27 \pm 10$ $36 \pm 6$ $f_k k_r$ isoeugenol2315 $4 \pm 4$ $n.d.$ $n.d.$ $n.d.$ $f_i$ $(E)$ -linalool oxide1428 $n.d.$ $n.d.$ $n.d.$ $f_i$  | aldehydes                         |                   |                     |                          |                        |         |
| nonanal**1391n.q. (b) $9 \pm 3$ (a) $5 \pm 0$ (a) $f_i^h$ prop-2-enal**843n.q. (b) $14 \pm 7$ (a)n.d. (b) $f_i$ propanal**801n.q. (b) $7 \pm 3$ (a)n.d. (b) $f_i$ benzaldehyde1516n.q.n.q.n.q.n.q. $f_i$ benzaldehyde1516n.q.n.q.n.q. $f_i$ 2-methylbutanal909n.q.n.d.n.d. $f_i$ 3-methylbutanal912n.q.n.d.n.d. $f_i$ 3-methylbutanal912n.q.n.d. $f_i$ benzalcehyne1317n.d.n.q. $n.d.$ $f_i$ c.(E)-hept-2-enal1317n.d. $f_i$ $f_i$ benzalcehyne1009 $20 \pm 4$ (b) $62 \pm 6$ (a) $49 \pm 9$ (a) $f_i^h$ octan-3-one1254n.q. $2 \pm 2$ $2 \pm 2$ $f_i^h$ acetophenone1640n.d.n.q. $n.d.$ $f_i$ oct1-en-3-one1296n.d.n.d. $n.d.$ $f_i$ (Z)-geranylacetone1859n.q.n.d. $n.d.$ $f_i$ idersUUS2 \pm 4 $27 \pm 10$ $36 \pm 6$ $f_i k_r$ isoeugenol2315 $4 \pm 4$ n.d.n.d. $f_i$ (E)-linalool oxide1428n.d.n.d. $n.d.$ $f_i$   | (E)-pent-2-enal                   | 1120              | $22 \pm 4$          | $36 \pm 10$              | $25 \pm 4$             | f,i     |
| prop-2-enal**843n.q. (b) $14 \pm 7$ (a)n.d. (b) $f_i$ propanal**801n.q. (b) $7 \pm 3$ (a)n.d. (b) $f_i$ benzaldehyde1516n.q. (b) $7 \pm 3$ (a)n.d. (b) $f_i$ benzaldehyde1516n.q. (b)n.q. (c)n.q. (c) $n.q.$ $n.q.$ $n.q.$ $(E,E)$ -hepta-2,4-dienal1475n.d.n.q. (c) $n.q.$ $n.q.$ $n.q.$ $n.q.$ $f_i$ 2-methylbutanal909n.q.n.d.n.d. $n.d.$ $f.d.$ $f_i$ 3-methylbutanal912n.q. $n.d.$ $n.d.$ $n.d.$ $f.d.$ $(E)$ -hept-2-enal1317 $n.d.$ $n.q.$ $n.d.$ $f.d.$ $(E)$ -hept-2-enal1317 $n.d.$ $n.q.$ $n.d.$ $f.d.$ $(E)$ -hept-3-one**1009 $20 \pm 4$ (b) $62 \pm 6$ (a) $49 \pm 9$ (a) $f.f.$ octan-3-one1254 $n.q.$ $2 \pm 2$ $2 \pm 2$ $f.f.$ acetophenone1640 $n.d.$ $n.q.$ $n.q.$ $f.f.$ oct-1-en-3-one1296 $n.d.$ $n.q.$ $n.d.$ $f.f.$ $(Z)$ -geranylacetone1859 $n.q.$ $n.d.$ $n.d.$ $f.f.$ <   | nonanal**                         | 1391              | n.q. (b)            | $9 \pm 3$ (a)            | $5 \pm 0$ (a)          | f,h     |
| $\begin{array}{ c c c c c c } propanal^{**} & 801 & n.q. (b) & 7 \pm 3 (a) & n.d. (b) & f,i \\ benzaldehyde & 1516 & n.q. & n.q. & n.q. & n.q. & f,n \\ benzaldehyde & 1516 & n.q. & n.q. & n.q. & n.q. & f,n \\ (E,E)-hepta-2,4-dienal & 1475 & n.d. & n.q. & n.q. & n.q. & f,i \\ 2-methylbutanal & 909 & n.q. & n.d. & n.d. & f,i \\ 3-methylbutanal & 912 & n.q. & n.d. & n.d. & f,i \\ 3-methylbutanal & 912 & n.q. & n.d. & n.d. & f,i \\ (E)-hept-2-enal & 1317 & n.d. & n.q. & n.d. & f,g,i \\ (E)-hept-3-one^{**} & 1009 & 20 \pm 4 (b) & 62 \pm 6 (a) & 49 \pm 9 (a) & f,h \\ octan-3-one & 1254 & n.q. & 2 \pm 2 & 2 \pm 2 & f,h \\ acetophenone & 1640 & n.d. & n.q. & n.d. & f,g,i \\ oct-1-en-3-one & 1296 & n.d. & n.q. & n.d. & f,i \\ (Z)-geranylacetone & 1859 & n.q. & n.d. & n.d. & f,i \\ (Z)-geranylacetone & 1859 & n.q. & n.d. & n.d. & f,i \\ isoeugenol & 2315 & 4 \pm 4 & n.d. & n.d. & n.d. & f,i \\ (E)-linalool oxide & 1428 & n.d. & n.d. & n.q. & j,k \\ \end{array}$  | prop-2-enal**                     | 843               | n.q. (b)            | $14 \pm 7 (a)$           | n.d. (b)               | f,i     |
| benzaldehyde1516n.q.n.q.n.q.n.q. $f,n$ $(E,E)$ -hepta-2,4-dienal1475n.d.n.q.n.q. $f,i$ 2-methylbutanal909n.q.n.d.n.d. $f,i$ 3-methylbutanal912n.q.n.d.n.d. $f,i$ $(E)$ -hept-2-enal1317n.d.n.q.n.d. $f,j$ $(E)$ -hept-2-enal1317n.d.n.q.n.d. $f,j$ $ketones$ $i$ $i$ $f,j$ $f,j$ $f,j$ octan-3-one**1009 $20 \pm 4$ (b) $62 \pm 6$ (a) $49 \pm 9$ (a) $f,j$ octan-3-one1254n.q. $2 \pm 2$ $2 \pm 2$ $f,j$ acetophenone1640n.d.n.q. $n.q.$ $f,j$ oct-1-en-3-one1296n.d.n.q. $n.d.$ $f,j$ menthone1457n.d.n.d. $n.q.$ $f,j$ $(Z)$ -geranylacetone1859 $n.q.$ $n.d.$ $n.d.$ $f,j$ others $V$ $V$ $V \pm 10$ $36 \pm 6$ $f,k,r$ isoeugenol2315 $4 \pm 4$ $n.d.$ $n.d.$ $n.d.$ $f,j$ $(E)$ -linalool oxide1428 $n.d.$ $n.d.$ $n.d.$ $n.d.$ $f,j$  | propanal**                        | 801               | n.q. (b)            | $7 \pm 3$ (a)            | n.d. (b)               | f,i     |
|  | benzaldehyde                      | 1516              | n.q.                | n.q.                     | n.q.                   | f,n     |
| 2-methylbutanal909n.q.n.d.n.d.n.d. $fi$ 3-methylbutanal912n.q.n.d.n.d. $fi$ $(E)$ -hept-2-enal1317n.d.n.q.n.d. $fg,i$ $ketones$ $ketones$ $ketones$ $ketones$ $ketones$ $ketones$ $ketones$ pent-1-en-3-one**1009 $20 \pm 4$ (b) $62 \pm 6$ (a) $49 \pm 9$ (a) $f_ih$ octan-3-one1254n.q. $2 \pm 2$ $2 \pm 2$ $f_ih$ acetophenone1640n.d.n.q.n.q. $f_ig,i$ oct-1-en-3-one1296n.d.n.q.n.d. $f_ih$ menthone1457n.d.n.d.n.d. $f_ih$ $(Z)$ -geranylacetone1859n.q. $r.d.$ $r.d.$ $f_i$ $others$ $S2 \pm 4$ $27 \pm 10$ $36 \pm 6$ $f_ik,r$ isoeugenol2315 $4 \pm 4$ n.d. $n.d.$ $f_i$ $(E)$ -linalool oxide1428n.d.n.d. $r.q.$ $f_ik$  | (E,E)-hepta-2,4-dienal            | 1475              | n.d.                | n.q.                     | n.q.                   | f,i     |
| 3-methylbutanal912n.q.n.d.n.d.n.d. $fi$ $(E)$ -hept-2-enal1317n.d.n.q.n.q.n.d. $fg,i$ $ketones$ $ketonesske$   | 2-methylbutanal                   | 909               | n.q.                | n.d.                     | n.d.                   | f,i     |
| (E)-hept-2-enal<br>ketones1317n.d.n.q.n.d.f.g.i $ketones$ pent-1-en-3-one**1009 $20 \pm 4$ (b) $62 \pm 6$ (a) $49 \pm 9$ (a) $f_ih$ octan-3-one1254n.q. $2 \pm 2$ $2 \pm 2$ $f_ih$ acetophenone1640n.d.n.q.n.q. $f_{g,i}$ oct-1-en-3-one1296n.d.n.q.n.d. $f_ih$ menthone1457n.d.n.d.n.q. $f_if$ (Z)-geranylacetone1859n.q.n.d. $n.d.$ $f_if$ othersS2 \pm 4 $27 \pm 10$ $36 \pm 6$ $f_ik,r$ isoeugenol2315 $4 \pm 4$ n.d.n.d. $n.q.$ (E)-linalool oxide1428n.d.n.d.n.q. $j_ik$   | 3-methylbutanal                   | 912               | n.q.                | n.d.                     | n.d.                   | f,i     |
| ketones         pent-1-en-3-one**       1009 $20 \pm 4$ (b) $62 \pm 6$ (a) $49 \pm 9$ (a) $f_h$ octan-3-one       1254       n.q. $2 \pm 2$ $2 \pm 2$ $f_{2}h$ acetophenone       1640       n.d.       n.q.       n.q. $f_{g,i}$ oct-1-en-3-one       1296       n.d.       n.q.       n.d. $f_{i}h$ menthone       1457       n.d.       n.d.       n.q. $f_{i}i$ (Z)-geranylacetone       1859       n.q.       n.d.       n.d. $f_{i}i$ others       V       V $32 \pm 4$ $27 \pm 10$ $36 \pm 6$ $f_{k,r}$ isoeugenol       2315 $4 \pm 4$ n.d.       n.d. $f_{i}i$ (E)-linalool oxide       1428       n.d.       n.d. $n.q.$ $f_{i}k$  | (E)-hept-2-enal                   | 1317              | n.d.                | n.q.                     | n.d.                   | f,g,i   |
| pent-1-en-3-one**1009 $20 \pm 4$ (b) $62 \pm 6$ (a) $49 \pm 9$ (a) $f_{ih}$ octan-3-one1254n.q. $2 \pm 2$ $2 \pm 2$ $f_{jh}$ acetophenone1640n.d.n.q.n.q. $f_{g,i}$ oct-1-en-3-one1296n.d.n.q.n.d. $f_{ih}$ menthone1457n.d.n.d.n.q. $f_{ih}$ (Z)-geranylacetone1859n.q.n.d.n.d. $f_{ih}$ others $C5$ -compounds963 $32 \pm 4$ $27 \pm 10$ $36 \pm 6$ $f_{ik}$ ,risoeugenol2315 $4 \pm 4$ n.d.n.d. $n.d.$ $f_{ih}$ (E)-linalool oxide1428n.d.n.d. $n.q.$ $j_{ik}$  | ketones                           |                   |                     |                          |                        |         |
| octan-3-one1254n.q. $2 \pm 2$ $2 \pm 2$ $f_{i}h$ acetophenone1640n.d.n.q.n.q. $f_{i}g_{i}i$ oct-1-en-3-one1296n.d.n.q.n.d. $f_{i}h$ menthone1457n.d.n.d.n.q. $f_{i}i$ (Z)-geranylacetone1859n.q.n.d.n.d. $f_{i}i$ others $C5$ -compounds963 $32 \pm 4$ $27 \pm 10$ $36 \pm 6$ $f_{i}k_{i}r$ isoeugenol2315 $4 \pm 4$ n.d.n.d. $f_{i}i$ (E)-linalool oxide1428n.d.n.d. $n.q.$ $j_{i}k$  | pent-1-en-3-one**                 | 1009              | $20 \pm 4$ (b)      | $62 \pm 6 (a)$           | $49 \pm 9 (a)$         | f,h     |
| acetophenone1640n.d.n.q.n.q.f.g.ioct-1-en-3-one1296n.d.n.q.n.d.f.hmenthone1457n.d.n.d.n.q.f.i(Z)-geranylacetone1859n.q.n.d.n.d.f.iothers $52 \pm 4$ $27 \pm 10$ $36 \pm 6$ f.k.risoeugenol2315 $4 \pm 4$ n.d.n.d.f.i(E)-linalool oxide1428n.d.n.d.n.q.j.k  | octan-3-one                       | 1254              | n.q.                | $2 \pm 2$                | $2 \pm 2$              | f,h     |
| oct-1-en-3-one1296n.d.n.q.n.d. $f_{,h}$ menthone1457n.d.n.d.n.q. $f_{,i}$ (Z)-geranylacetone1859n.q.n.d.n.d. $f_{,i}$ others $C5$ -compounds963 $32 \pm 4$ $27 \pm 10$ $36 \pm 6$ $f_{,k,r}$ isoeugenol2315 $4 \pm 4$ n.d.n.d. $f_{,i}$ (E)-linalool oxide1428n.d.n.d.n.q. $j_{,k}$  | acetophenone                      | 1640              | n.d.                | n.q.                     | n.q.                   | f,g,i   |
| menthone1457n.d.n.d.n.q. $f_i$ (Z)-geranylacetone1859n.q.n.d.n.d. $f_i$ others $cf_i$ $f_i$ $f_i$ $f_i$ C5-compounds963 $32 \pm 4$ $27 \pm 10$ $36 \pm 6$ $f_i$ k,risoeugenol2315 $4 \pm 4$ n.d.n.d. $f_i$ (E)-linalool oxide1428n.d.n.d.n.q. $j_i$ k  | oct-1-en-3-one                    | 1296              | n.d.                | n.q.                     | n.d.                   | f,h     |
| (Z)-geranylacetone       1859       n.q.       n.d.       n.d. $f_i$ others $f_i$ C5-compounds       963 $32 \pm 4$ $27 \pm 10$ $36 \pm 6$ $f_i k, r$ isoeugenol       2315 $4 \pm 4$ n.d.       n.d. $f_i$ (E)-linalool oxide       1428       n.d.       n.d.       n.q. $j_i k$   | menthone                          | 1457              | n.d.                | n.d.                     | n.q.                   | f,i     |
| others           C5-compounds         963 $32 \pm 4$ $27 \pm 10$ $36 \pm 6$ $f_ik,r$ isoeugenol         2315 $4 \pm 4$ n.d.         n.d. $f_{ji}$ (E)-linalool oxide         1428         n.d.         n.d.         n.q. $j_ik$  | (Z)-geranylacetone                | 1859              | n.q.                | n.d.                     | n.d.                   | f,i     |
| C5-compounds         963 $32 \pm 4$ $27 \pm 10$ $36 \pm 6$ $f_{jk},r$ isoeugenol         2315 $4 \pm 4$ n.d.         n.d. $f_{ji}$ (E)-linalool oxide         1428         n.d.         n.d.         n.q. $j_{jk}$   | others                            |                   |                     |                          |                        |         |
| isoeugenol       2315 $4 \pm 4$ n.d.       n.d. $f_{,i}$ (E)-linalool oxide       1428       n.d.       n.d.       n.q. $j_{,k}$   | C5-compounds                      | 963               | $32 \pm 4$          | $27 \pm 10$              | $36 \pm 6$             | f,k,r   |
| (E)-linalool oxide 1428 n.d. n.d. n.q. j,k   | isoeugenol                        | 2315              | $4 \pm 4$           | n.d.                     | n.d.                   | f,i     |
|  | (E)-linalool oxide                | 1428              | n.d.                | n.d.                     | n.q.                   | j,k     |

<sup>*a*</sup>Correlation analysis was carried out by ANOVA. Levels of significance: p = 0-0.001: highly significant (\*\*\*), p = 0.001-0.01: very significant (\*\*), p = 0.01-0.05: significant (\*); statistically significant differences (Tukey's HSC) are indicated by different characters (a,b and c). <sup>*c*</sup>Material harvested on 03 July, 2011. <sup>*c*</sup>Material harvested on 04 July, 2011. <sup>*b*</sup>Linear retention indices. <sup>*d*</sup>Data from triplicate experiments for each batch: mean  $\pm$  standard deviation. <sup>*f*</sup>Identification based on comparison of mass spectral and GC data with those of authentic reference compounds. <sup>*g*</sup>Recovery considered. <sup>*h*</sup>Reference compound from Aldrich, Steinheim, Germany. <sup>*i*</sup>Reference compound provided by *Frey+Lau GmbH*, Henstedt-Ulzburg, Germany. <sup>*j*</sup>Tentatively identified by comparison of mass spectral data with those from database. <sup>*k*</sup>Quantitation without response factor. <sup>*l*</sup>Not quantifiable: concentration below limit of quantitation (1.7  $\mu$ g/kg). <sup>*m*</sup>Not detectable: concentration below limit of identification (0.6  $\mu$ g/kg). <sup>*n*</sup>Reference on (2,3-di-O-acetyl-6-O-*tert*-butyldimethylsilyl)- $\beta$ -cyclodextrin as chiral stationary phase. <sup>*p*</sup>The ratio of enantiomers was identified by comparison of retention times with an authentic reference on (2,3-di-O-acetyl-6-O-*tert*-butyldimethylsilyl)- $\beta$ -cyclodextrin as chiral stationary phase. <sup>*p*</sup>The ratio of enantiomers was identified by comparison of retention times with an authentic reference on (2,3-di-O-acetyl-6-O-*tert*-butyldimethylsilyl)- $\beta$ -cyclodextrin as chiral stationary phase. <sup>*p*</sup>Coelution of propyl acetate, pentan-2-one, pentan-3-one and pentanal.

Germany) and *n*-pentane (AppliChem., Darmstadt, Germany) were distilled before use.

Isolation of Volatiles by Vacuum Headspace Extraction (VHS). Before analysis, stored fruits were brought to room temperature (approximately 2 h). After removal of the peduncles, 500 g of jostaberries were homogenized (Moulinex Turbo blender) with 400 mL water for 30 s. After the addition of 150  $\mu$ g of heptan-2-ol as internal standard (1 mL of a 1:10-diluted stock solution of 0.150 g

heptan-2-ol/100 mL water), the homogenate was transferred into a 2 L round-bottom flask and the blender was rinsed with 150 mL of water. The flask was placed into a water bath (35 °C) and the isolation was carried out for 2 h at a vacuum of 1–10 mbar (Leybold-Hereus pump, typ D4A). The aqueous distillate was condensed in three cooling traps. The first two were cooled by a water–ice mixture and the third by liquid nitrogen. After thawing, the distillates were pooled and extracted (3 × 50 mL) using a mixture of diethyl ether and

| compounds2010 (july 19) [µg/kg]2011 (july 13) [µg/kg]2012 (july 16) [µg/kg]( $E$ )-hex-2-cnal8066 ± 1099613 ± 81911473 ± 2730( $Z$ )-hex-3-enal652 ± 142565 ± 226322 ± 198( $E$ )-hex-2-en1-0862 ± 325525 ± 180438 ± 151hexanal*158 ± 33 (b)365 ± 75 (a)330 ± 114 (ab)( $Z$ )-hex-3-en1-01***223 ± 19(a)186 ± 11 (a)127 ± 13 (b)( $E$ )-hex-3-en1149 ± 74233 ± 22160 ± 30( $Z$ )-hex-3-en1149 ± 74233 ± 1035 ± 3( $E$ )-hex-3-en1-0145 ± 1043 ± 1035 ± 3( $E$ )-hex-3-en1-01***68 ± 16 (a)43 ± 1035 ± 3( $E$ )-hex-3-en1-01**34 ± 14 (a)25 ± 33 (ab)8 ± 7 (b)total:1002561160112921methyl butanoate***695 ± 225 (b)2330 ± 291 (a)2000 ± 287 (a)methyl butanoate***106 ± 16 (a)13 ± 3 (a)34 ± 10 (b)methyl butanoate***125 (b)40 ± 3 (a)24 ± 1 (b)methyl beznoate***100 ± 16 (a)13 ± 26151 ± 31(a)methyl beznoate***23 ± 5 (b)40 ± 3 (a)24 ± 1 (b)methyl beznoate***23 ± 97308 ± 51484 ± 80methyl beznoate***24 ± 1 (c)22 ± 4 (b)62 ± 9 (a)total:1018287928672-methylbut-3-en-2-01*586 ± 74 (b)1670 ± 548 (a)1378 ± 197 (a,b)1,8-cincel453 ± 97308 ± 51484 ± 80pent-1-en-3-one*28 ± 2 (b)   |                             | Freising               |                        |                        |  |  |
|--|-----------------------------|------------------------|------------------------|------------------------|--|--|
| (E)-hex-2-enal $8066 \pm 109$ $9613 \pm 819$ $11473 \pm 2730$ (Z)-hex-3-enal $652 \pm 142$ $565 \pm 226$ $322 \pm 198$ (E)-hex-2-en-1-ol $862 \pm 325$ $525 \pm 180$ $438 \pm 151$ hexanal* $158 \pm 33$ (b) $365 \pm 75$ (a) $330 \pm 114$ (ab)(Z)-hex-3-en-1-ol*** $223 \pm 19(a)$ $186 \pm 11$ (a) $127 \pm 13$ (b)(E)-hex-3-enal $149 \pm 74$ $233 \pm 22$ $160 \pm 30$ (Z)-hex-2-enal** $68 \pm 16$ (a) $45 \pm 4$ (ab) $30 \pm 3$ (b)hexan-1-ol $45 \pm 10$ $43 \pm 10$ $35 \pm 3$ (E)-hex-3-en-1-ol* $45 \pm 10$ $43 \pm 10$ $35 \pm 3$ (E)-hex-3-en-1-ol* $45 \pm 10$ $43 \pm 10$ $35 \pm 3$ (E)-hex-3-en-1-ol* $45 \pm 10$ $43 \pm 10$ $35 \pm 3$ (E)-hex-3-en-1-ol* $45 \pm 10$ $43 \pm 10$ $35 \pm 3$ (E)-hex-2-enal*** $695 \pm 225$ (b) $2330 \pm 291$ (a) $2000 \pm 287$ (a)methyl butanoate*** $695 \pm 225$ (b) $2330 \pm 291$ (a) $2000 \pm 287$ (a)methyl butanoate*** $695 \pm 225$ (b) $2330 \pm 291$ (a) $2000 \pm 287$ (a)methyl butanoate*** $160 \pm 16$ (a) $13 \pm 3$ (b) $31 \pm 10$ (b)methyl benzoate*** $160 \pm 16$ (a) $13 \pm 3$ (b) $34 \pm 10$ (b)methyl benzoate*** $103 \pm 5$ $44 \pm 10$ $22 \pm 9$ (a)total: $1018$ $2879$ $2867$ 2-methylbut-3-en-2.ol* $286 \pm 74$ (b) $1670 \pm 548$ (a) $178 \pm 197$ (ab) $1,8 \pm 10$ $453 \pm 97$ $38 \pm 51$ $484 \pm 80$ pent-1-en-3-one*<   | compounds                   | 2010 (July 19) [µg/kg] | 2011 (July 13) [µg/kg] | 2012 (July 16) [µg/kg] |  |  |
|  | (E)-hex-2-enal              | 8066 ± 109             | 9613 ± 819             | $11473 \pm 2730$       |  |  |
| (E)-hex-2-en-1-ol $862 \pm 325$ $525 \pm 180$ $438 \pm 151$ hexanal*158 $\pm$ 33 (b) $365 \pm 75$ (a) $330 \pm 114$ (a,b)(Z)-hex-3-en-1-ol*** $223 \pm 19(a)$ $186 \pm 11$ (a) $127 \pm 13$ (b)(E)-hex-3-enal $149 \pm 74$ $233 \pm 22$ $160 \pm 30$ (Z)-hex-2-enal** $68 \pm 16$ (a) $45 \pm 4$ (a,b) $30 \pm 3$ (b)hexan-1-ol $45 \pm 10$ $43 \pm 10$ $35 \pm 3$ (E)-hex-3-en-1-ol* $45 \pm 10$ $43 \pm 10$ $55 \pm 3$ (E)-hex-3-en-1-ol* $45 \pm 10$ $43 \pm 10$ $25 \pm 3$ (a,b)total:102561160112921methyl butanoate*** $695 \pm 225$ (b) $2330 \pm 291$ (a) $2000 \pm 287$ (a)ethyl butanoate*** $695 \pm 202$ (c) $348 \pm 66$ (b) $596 \pm 149$ (a)methyl (E)-but-2-enoate* $90 \pm 4$ (b) $125 \pm 15$ (a,b) $34 \pm 10$ (b)methyl benzoate*** $160 \pm 16$ (a) $13 \pm 3$ (b) $34 \pm 10$ (b)methyl benzoate*** $23 \pm 5$ (b) $40 \pm 3$ (a) $24 \pm 1$ (b)ethyl (E)-but-2-enoate*** $106 \pm 16$ (a) $13 \pm 3$ (b) $34 \pm 10$ (b)methyl benzoate*** $23 \pm 5$ (b) $40 \pm 3$ (a) $24 \pm 1$ (b)methyl benzoate*** $23 \pm 5$ (b) $40 \pm 3$ (a) $24 \pm 1$ (b)methyl benzoate*** $58 \pm 1$ (b) $1670 \pm 548$ (a) $1378 \pm 197$ (a,b)hethyl benzoate*** $23 \pm 5$ (b) $1670 \pm 548$ (a) $1378 \pm 197$ (a,b)hethyl (R)-oct-1-en-3-ol*** $28 \pm 2$ (b) $57 \pm 10$ (a) $49 \pm 12$ (a,b)(R)-oct-1-en-3-ol*** $28 \pm 2$ (b) <td>(Z)-hex-3-enal</td> <td><math>652 \pm 142</math></td> <td><math>565 \pm 226</math></td> <td><math>322 \pm 198</math></td> | (Z)-hex-3-enal              | $652 \pm 142$          | $565 \pm 226$          | $322 \pm 198$          |  |  |
| hexanal*158 ± 33 (b) $365 \pm 75$ (a) $330 \pm 114$ (a,b)(Z)-hex-3-en-1-ol*** $223 \pm 19(a)$ $186 \pm 11$ (a) $127 \pm 13$ (b)(E)-hex-3-enal $149 \pm 74$ $233 \pm 22$ $160 \pm 30$ (Z)-hex-2-enal** $68 \pm 16$ (a) $45 \pm 4$ (a,b) $30 \pm 3$ (b)hexan-1-ol $45 \pm 10$ $43 \pm 10$ $35 \pm 3$ (E)-hex-3-en-1-ol* $45 \pm 10$ $43 \pm 10$ $35 \pm 3$ (E)-hex-3-en-1-ol* $34 \pm 14$ (a) $25 \pm 3$ (a,b) $8 \pm 7$ (b)total:102261160112921methyl butanoate*** $695 \pm 225$ (b) $2330 \pm 291$ (a) $2000 \pm 287$ (a)ethyl butanoate*** $695 \pm 225$ (b) $2330 \pm 291$ (a) $2000 \pm 287$ (a)methyl butanoate*** $695 \pm 225$ (b) $2330 \pm 291$ (a) $2000 \pm 287$ (a)methyl butanoate*** $90 \pm 4$ (b) $125 \pm 15$ (a,b) $151 \pm 31(a)$ methyl (E)-but-2-enoate* $90 \pm 4$ (b) $125 \pm 15$ (a,b) $34 \pm 10$ (b)methyl hexanoate*** $23 \pm 5$ (b) $40 \pm 3$ (a) $24 \pm 1$ (b)ethyl (E)-but-2-enoate*** $4 \pm 1(c)$ $22 \pm 4$ (b) $62 \pm 9$ (a)total:1018287928672-methylbut-3-en-2-ol* $88 \pm 74$ (b) $1670 \pm 548$ (a) $1378 \pm 197$ (a,b)1,8-cineol $453 \pm 97$ $308 \pm 51$ $484 \pm 80$ pent-1-en-3-one* $28 \pm 2$ (b) $57 \pm 10$ (a) $49 \pm 12$ (a,b)(R)-ort-1-en-3-ol*** $5 \pm 1$ (b) $63 \pm 16$ (a) $10 \pm 3$ (b)(R)-ort-1-en-3-ol*** $5 \pm 1$ (b) $27 \pm 3$ (a) $17 \pm 1$ (a) <td>(<i>E</i>)-hex-2-en-1-ol</td> <td><math>862 \pm 325</math></td> <td><math>525 \pm 180</math></td> <td><math>438 \pm 151</math></td>              | ( <i>E</i> )-hex-2-en-1-ol  | $862 \pm 325$          | $525 \pm 180$          | $438 \pm 151$          |  |  |
| (Z)-hex-3-en-1-ol***223 $\pm 19(a)$ 186 $\pm 11(a)$ 127 $\pm 13 (b)$ (Z)-hex-3-enal149 $\pm 74$ 233 $\pm 22$ 160 $\pm 30$ (Z)-hex-2-enal**68 $\pm 16(a)$ 45 $\pm 4(ab)$ 30 $\pm 3(b)$ hexan-1-ol45 $\pm 10$ 43 $\pm 10$ 35 $\pm 3$ (E)-hex-3-en-1-ol*34 $\pm 14(a)$ 25 $\pm 3(a,b)$ 8 $\pm 7(b)$ total:102561160112921methyl butanoate***695 $\pm 225 (b)$ 2330 $\pm 291(a)$ 2000 $\pm 287(a)$ ethyl butanoate***46 $\pm 20(c)$ 348 $\pm 66(b)$ 596 $\pm 149(a)$ methyl (E)-but-2-enoate*90 $\pm 4(b)$ 125 $\pm 15(a,b)$ 151 $\pm 31(a)$ methyl beznoate***160 $\pm 16(a)$ 13 $\pm 3(b)$ 34 $\pm 10(b)$ methyl (E)-but-2-enoate*90 $\pm 4(b)$ 125 $\pm 15(a,b)$ 151 $\pm 31(a)$ methyl (E)-but-2-enoate***160 $\pm 16(a)$ 13 $\pm 3(b)$ 34 $\pm 10(b)$ methyl (E)-but-2-enoate***4 $\pm 1(c)$ 22 $\pm 4(b)$ 62 $\pm 9(a)$ total:1018287928672-methylbut-3-en-2-ol*586 $\pm 74(b)$ 1670 $\pm 548(a)$ 1378 $\pm 197(a,b)$ 1,8-cineol453 $\pm 97$ 308 $\pm 51$ 484 $\pm 80$ pent-1-en-3-one*28 $\pm 2(b)$ 57 $\pm 10(a)$ 49 $\pm 12(a,b)$ (R)-oct-1-en-3-ol**28 $\pm 2(b)$ 57 $\pm 10(a)$ 192 $\pm 3(a)$ (C)-pent-2-enal29 $\pm 3$ 30 $\pm 7$ 22 $\pm 3$ (C)-pent-2-enal29 $\pm 3$ 30 $\pm 7$ 22 $\pm 3$ (C)-pent-2-enal22 $\pm 6(a)$ 14 $\pm 5(a,b)$ 10 $\pm 2(b)$ total:11532195<   | hexanal*                    | $158 \pm 33$ (b)       | $365 \pm 75$ (a)       | $330 \pm 114$ (a,b)    |  |  |
| (E)-hex-3-enal $149 \pm 74$ $233 \pm 22$ $160 \pm 30$ (Z)-hex-2-enal** $68 \pm 16$ (a) $45 \pm 4$ (ab) $30 \pm 3$ (b)hexan-1-ol $45 \pm 10$ $43 \pm 10$ $35 \pm 3$ (E)-hex-3-en-1-ol* $34 \pm 14$ (a) $25 \pm 3$ (ab) $8 \pm 7$ (b)total:102561160112921methyl butanoate*** $695 \pm 225$ (b) $2330 \pm 291$ (a) $2000 \pm 287$ (a)ethyl butanoate*** $46 \pm 20$ (c) $348 \pm 66$ (b) $596 \pm 149$ (a)methyl (b)-but-2-enoate* $90 \pm 4$ (b) $125 \pm 15$ (ab) $151 \pm 31(a)$ methyl bezoate*** $160 \pm 16$ (a) $13 \pm 3$ (b) $34 \pm 10$ (b)methyl bezoate*** $160 \pm 16$ (a) $13 \pm 3$ (b) $34 \pm 10$ (b)methyl (b)-but-2-enoate* $23 \pm 5$ (b) $40 \pm 3$ (a) $24 \pm 1$ (b)ethyl (b)-but-2-enoate*** $4 \pm 1(c)$ $22 \pm 4$ (b) $62 \pm 9$ (a)total:1018287928672-methylbut-3-en-2-ol* $586 \pm 74$ (b) $1670 \pm 548$ (a) $1378 \pm 197$ (a,b)1,8-cineol $453 \pm 97$ $308 \pm 51$ $484 \pm 80$ pent-1-en-3-one* $28 \pm 2$ (b) $57 \pm 10$ (a) $49 \pm 12$ (a,b)(R)-ort-1-en-3-ol*** $5 \pm 1$ (b) $68 \pm 16$ (a) $10 \pm 3$ (b)(E)-pent-2-enal $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ (Z)-pent-2-en-1-ol*** $22 \pm 1(b)$ $27 \pm 3$ (a) $18 \pm 1$ (b)pent-1-en-3-ol*** $8 \pm 2$ (b) $21 \pm 3$ (a) $17 \pm 1$ (a)terpinen-4-ol* $22 \pm 6$ (a) $14 \pm 5$ (a,b) $10 \pm 2$ (b)total: <td< th=""><td>(Z)-hex-3-en-1-ol***</td><td><math>223 \pm 19(a)</math></td><td><math>186 \pm 11</math> (a)</td><td><math>127 \pm 13</math> (b)</td></td<>               | (Z)-hex-3-en-1-ol***        | $223 \pm 19(a)$        | $186 \pm 11$ (a)       | $127 \pm 13$ (b)       |  |  |
| (Z)-hex-2-enal** $68 \pm 16 (a)$ $45 \pm 4 (ab)$ $30 \pm 3 (b)$ hexan-1-ol $45 \pm 10$ $43 \pm 10$ $35 \pm 3$ (E)-hex-3-en-1-ol* $34 \pm 14 (a)$ $25 \pm 3 (ab)$ $8 \pm 7 (b)$ total: $10256$ $11601$ $12921$ methyl butanoate*** $695 \pm 225 (b)$ $2330 \pm 291 (a)$ $2000 \pm 287 (a)$ ethyl butanoate*** $695 \pm 225 (b)$ $2330 \pm 291 (a)$ $2000 \pm 287 (a)$ methyl butanoate*** $695 \pm 225 (b)$ $2330 \pm 291 (a)$ $2000 \pm 287 (a)$ methyl butanoate*** $46 \pm 20 (c)$ $348 \pm 66 (b)$ $596 \pm 149 (a)$ methyl bezoate*** $160 \pm 16 (a)$ $125 \pm 15 (ab)$ $151 \pm 31(a)$ methyl beznoate*** $160 \pm 16 (a)$ $13 \pm 3 (b)$ $34 \pm 10 (b)$ methyl beznoate*** $23 \pm 5 (b)$ $40 \pm 3 (a)$ $24 \pm 1 (b)$ ethyl (E)-but-2-enoate*** $23 \pm 5 (b)$ $1670 \pm 548 (a)$ $1378 \pm 197 (a,b)$ $1,8$ -cincol $453 \pm 97$ $308 \pm 51$ $484 \pm 80$ pent-1-en-3-ol** $586 \pm 74 (b)$ $1670 \pm 548 (a)$ $1378 \pm 197 (a,b)$ $1,8$ -cincol $28 \pm 2 (b)$ $57 \pm 10 (a)$ $49 \pm 12 (a,b)$ (R)-ort-1-en-3-ol** $28 \pm 2 (b)$ $57 \pm 10 (a)$ $49 \pm 12 (a,b)$ (E)-pent-2-enal $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ (Z)-pent-2-enal $22 \pm 1(b)$ $27 \pm 3 (a)$ $18 \pm 1 (b)$ pent-1-en-3-ol*** $8 \pm 2 (b)$ $21 \pm 3 (a)$ $17 \pm 1 (a)$ terpinen-4-ol* $22 \pm 6 (a)$ $14 \pm 5 (a,b)$ $10 \pm 2 (b)$ total: $153$ $1262$ $196$   | (E)-hex-3-enal              | $149 \pm 74$           | $233 \pm 22$           | $160 \pm 30$           |  |  |
| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $  | (Z)-hex-2-enal**            | $68 \pm 16$ (a)        | $45 \pm 4 (a,b)$       | $30 \pm 3$ (b)         |  |  |
| (E)-hex-3-en-1-ol* $34 \pm 14$ (a) $25 \pm 3$ (a,b) $8 \pm 7$ (b)total:102561160112921methyl butanoate*** $695 \pm 225$ (b) $2330 \pm 291$ (a) $2000 \pm 287$ (a)ethyl butanoate*** $46 \pm 20$ (c) $348 \pm 66$ (b) $596 \pm 149$ (a)methyl (E)-but-2-enoate* $90 \pm 4$ (b) $125 \pm 15$ (a,b) $151 \pm 31(a)$ methyl benzoate*** $160 \pm 16$ (a) $13 \pm 3$ (b) $34 \pm 10$ (b)methyl benzoate*** $23 \pm 5$ (b) $40 \pm 3$ (a) $24 \pm 1$ (b)ethyl (E)-but-2-enoate*** $4 \pm 1(c)$ $22 \pm 4$ (b) $62 \pm 9$ (a)total:1018287928672-methylbut-3-en-2-ol* $586 \pm 74$ (b) $1670 \pm 548$ (a) $1378 \pm 197$ (a,b)1,8-cineol $453 \pm 97$ $308 \pm 51$ $484 \pm 80$ pent-1-en-3-one* $28 \pm 2$ (b) $57 \pm 10$ (a) $49 \pm 12$ (a,b)(R)-oct-1-en-3-ol*** $5 \pm 1$ (b) $68 \pm 16$ (a) $10 \pm 3$ (b)(E)-pent-2-enal $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ (Z)-pent-2-enal-ol** $22 \pm 1(b)$ $27 \pm 3$ (a) $18 \pm 1$ (b)pent-1-en-3-ol*** $8 \pm 2$ (b) $21 \pm 3$ (a) $17 \pm 1$ (a)terpinen-4-ol* $22 \pm 6$ (a) $14 \pm 5$ (a,b) $10 \pm 2$ (b)total:115319881988   | hexan-1-ol                  | $45 \pm 10$            | $43 \pm 10$            | $35 \pm 3$             |  |  |
| total:102561160112921methyl butanoate*** $695 \pm 225$ (b) $330 \pm 291$ (a) $2000 \pm 287$ (a)ethyl butanoate*** $695 \pm 20$ (c) $348 \pm 66$ (b) $596 \pm 149$ (a)methyl [D)-but-2-enoate* $90 \pm 4$ (b) $125 \pm 15$ (a,b) $151 \pm 31(a)$ methyl benzoate*** $160 \pm 16$ (a) $13 \pm 3$ (b) $34 \pm 10$ (b)methyl benzoate*** $23 \pm 5$ (b) $40 \pm 3$ (a) $24 \pm 1$ (b)ethyl (E)-but-2-enoate*** $4 \pm 1(c)$ $22 \pm 4$ (b) $62 \pm 9$ (a)total:101828792867Comethylbut-3-en-2-ol*s $86 \pm 74$ (b) $1670 \pm 548$ (a) $1378 \pm 197$ (a,b)1,8-cineol $453 \pm 97$ $308 \pm 51$ $484 \pm 80$ pent-1-en-3-one* $28 \pm 2$ (b) $57 \pm 10$ (a) $49 \pm 12$ (a,b)(R)-oct-1-en-3-ol*** $5 \pm 1$ (b) $68 \pm 16$ (a) $10 \pm 3$ (b)(E)-pent-2-enal $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ (Z)-pent-2-enal $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ (Z)-pent-2-enal-ol*** $8 \pm 2$ (b) $27 \pm 3$ (a) $18 \pm 1$ (b)pent-1-en-3-ol*** $8 \pm 2$ (b) $21 \pm 3$ (a) $17 \pm 1$ (a)terpinen-4-ol* $22 \pm 6$ (a) $14 \pm 5$ (a,b) $10 \pm 2$ (b)total:untotal:1531988sum total:124271667517776  | ( <i>E</i> )-hex-3-en-1-ol* | $34 \pm 14$ (a)        | $25 \pm 3 (a,b)$       | $8 \pm 7$ (b)          |  |  |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$   | total:                      | 10256                  | 11601                  | 12921                  |  |  |
| ethyl butanoate*** $46 \pm 20 (c)$ $348 \pm 66 (b)$ $596 \pm 149 (a)$ methyl (E)-but-2-enoate* $90 \pm 4 (b)$ $125 \pm 15 (a,b)$ $151 \pm 31(a)$ methyl benzoate*** $160 \pm 16 (a)$ $13 \pm 3 (b)$ $34 \pm 10 (b)$ methyl hexanoate*** $23 \pm 5 (b)$ $40 \pm 3 (a)$ $24 \pm 1 (b)$ ethyl (E)-but-2-enoate*** $4 \pm 1(c)$ $22 \pm 4 (b)$ $62 \pm 9 (a)$ total:101828792867Total:2-methylbut-3-en-2-ol* $586 \pm 74 (b)$ $1670 \pm 548 (a)$ $1378 \pm 197 (a,b)$ 1,8-cineol $453 \pm 97$ $308 \pm 51$ $484 \pm 80$ pent-1-en-3-one* $28 \pm 2 (b)$ $57 \pm 10 (a)$ $49 \pm 12 (a,b)$ (R)-oct-1-en-3-ol*** $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ (Z)-pent-2-enal $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ (Z)-pent-2-enal-lol** $8 \pm 2 (b)$ $21 \pm 3 (a)$ $17 \pm 1 (a)$ pent-1-en-3-ol*** $8 \pm 2 (b)$ $21 \pm 3 (a)$ $17 \pm 1 (a)$ terpinen-4-ol* $22 \pm 6 (a)$ $14 \pm 5 (a,b)$ $10 \pm 2 (b)$ total:115321951988  | methyl butanoate***         | 695 ± 225 (b)          | $2330 \pm 291$ (a)     | $2000 \pm 287$ (a)     |  |  |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$   | ethyl butanoate***          | $46 \pm 20 (c)$        | $348 \pm 66$ (b)       | $596 \pm 149$ (a)      |  |  |
| methyl benzoate*** $160 \pm 16$ (a) $13 \pm 3$ (b) $34 \pm 10$ (b)methyl hexanoate*** $23 \pm 5$ (b) $40 \pm 3$ (a) $24 \pm 1$ (b)ethyl (E)-but-2-enoate*** $4 \pm 1$ (c) $22 \pm 4$ (b) $62 \pm 9$ (a)total:1018287928672-methylbut-3-en-2-ol* $586 \pm 74$ (b) $1670 \pm 548$ (a) $1378 \pm 197$ (a,b)1,8-cineol $453 \pm 97$ $308 \pm 51$ $484 \pm 80$ pent-1-en-3-one* $28 \pm 2$ (b) $57 \pm 10$ (a) $49 \pm 12$ (a,b)(R)-oct-1-en-3-ol*** $5 \pm 1$ (b) $68 \pm 16$ (a) $10 \pm 3$ (b)(E)-pent-2-enal $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ (Z)-pent-2-enal-1-ol** $22 \pm 1$ (b) $27 \pm 3$ (a) $18 \pm 1$ (b)pent-1-en-3-ol*** $8 \pm 2$ (b) $21 \pm 3$ (a) $17 \pm 1$ (a)terpinen-4-ol* $22 \pm 6$ (a) $14 \pm 5$ (a,b) $10 \pm 2$ (b)total:115321951988   | methyl (E)-but-2-enoate*    | $90 \pm 4$ (b)         | $125 \pm 15 (a,b)$     | $151 \pm 31(a)$        |  |  |
| methyl hexanoate*** $23 \pm 5$ (b) $40 \pm 3$ (a) $24 \pm 1$ (b)ethyl (E)-but-2-enoate*** $4 \pm 1$ (c) $22 \pm 4$ (b) $62 \pm 9$ (a)total:1018287928672-methylbut-3-en-2-ol* $586 \pm 74$ (b) $1670 \pm 548$ (a) $1378 \pm 197$ (a,b)1,8-cineol $453 \pm 97$ $308 \pm 51$ $484 \pm 80$ pent-1-en-3-one* $28 \pm 2$ (b) $57 \pm 10$ (a) $49 \pm 12$ (a,b)(R)-oct-1-en-3-ol*** $5 \pm 1$ (b) $68 \pm 16$ (a) $10 \pm 3$ (b)(E)-pent-2-enal $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ (Z)-pent-2-en-1-ol** $22 \pm 1$ (b) $27 \pm 3$ (a) $18 \pm 1$ (b)pent-1-en-3-ol*** $8 \pm 2$ (b) $21 \pm 3$ (a) $17 \pm 1$ (a)terpinen-4-ol* $22 \pm 6$ (a) $14 \pm 5$ (a,b) $10 \pm 2$ (b)total:115321951988   | methyl benzoate***          | $160 \pm 16$ (a)       | $13 \pm 3$ (b)         | $34 \pm 10$ (b)        |  |  |
| ethyl (E)-but-2-enoate*** $4 \pm 1(c)$ $22 \pm 4$ (b) $62 \pm 9$ (a)total:1018287928672-methylbut-3-en-2-ol* $586 \pm 74$ (b) $1670 \pm 548$ (a) $1378 \pm 197$ (a,b)1,8-cineol $453 \pm 97$ $308 \pm 51$ $484 \pm 80$ pent-1-en-3-one* $28 \pm 2$ (b) $57 \pm 10$ (a) $49 \pm 12$ (a,b)(R)-oct-1-en-3-ol*** $5 \pm 1$ (b) $68 \pm 16$ (a) $10 \pm 3$ (b)(E)-pent-2-enal $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ (Z)-pent-2-en-1-ol** $22 \pm 1$ (b) $27 \pm 3$ (a) $18 \pm 1$ (b)pent-1-en-3-ol*** $8 \pm 2$ (b) $21 \pm 3$ (a) $17 \pm 1$ (a)terpinen-4-ol* $22 \pm 6$ (a) $14 \pm 5$ (a,b) $10 \pm 2$ (b)total:115321951988  | methyl hexanoate***         | $23 \pm 5$ (b)         | $40 \pm 3 (a)$         | $24 \pm 1$ (b)         |  |  |
| total:1018287928672-methylbut-3-en-2-ol* $586 \pm 74$ (b) $1670 \pm 548$ (a) $1378 \pm 197$ (a,b)1,8-cineol $453 \pm 97$ $308 \pm 51$ $484 \pm 80$ pent-1-en-3-one* $28 \pm 2$ (b) $57 \pm 10$ (a) $49 \pm 12$ (a,b)(R)-oct-1-en-3-ol*** $5 \pm 1$ (b) $68 \pm 16$ (a) $10 \pm 3$ (b)(E)-pent-2-enal $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ (Z)-pent-2-en-1-ol** $22 \pm 1$ (b) $27 \pm 3$ (a) $18 \pm 1$ (b)pent-1-en-3-ol*** $8 \pm 2$ (b) $21 \pm 3$ (a) $17 \pm 1$ (a)terpinen-4-ol* $22 \pm 6$ (a) $14 \pm 5$ (a,b) $10 \pm 2$ (b)total:115321951988  | ethyl (E)-but-2-enoate***   | $4 \pm 1(c)$           | $22 \pm 4$ (b)         | $62 \pm 9 (a)$         |  |  |
| 2-methylbut-3-en-2-ol* $586 \pm 74$ (b) $1670 \pm 548$ (a) $1378 \pm 197$ (a,b) $1,8$ -cineol $453 \pm 97$ $308 \pm 51$ $484 \pm 80$ pent-1-en-3-one* $28 \pm 2$ (b) $57 \pm 10$ (a) $49 \pm 12$ (a,b) $(R)$ -oct-1-en-3-ol*** $5 \pm 1$ (b) $68 \pm 16$ (a) $10 \pm 3$ (b) $(E)$ -pent-2-enal $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ $(Z)$ -pent-2-en-1-ol** $22 \pm 1$ (b) $27 \pm 3$ (a) $18 \pm 1$ (b)pent-1-en-3-ol*** $8 \pm 2$ (b) $21 \pm 3$ (a) $17 \pm 1$ (a)terpinen-4-ol* $22 \pm 6$ (a) $14 \pm 5$ (a,b) $10 \pm 2$ (b)total:115321951988   | total:                      | 1018                   | 2879                   | 2867                   |  |  |
| 1,8-cineol $453 \pm 97$ $308 \pm 51$ $484 \pm 80$ pent-1-en-3-one* $28 \pm 2$ (b) $57 \pm 10$ (a) $49 \pm 12$ (a,b)(R)-oct-1-en-3-ol*** $5 \pm 1$ (b) $68 \pm 16$ (a) $10 \pm 3$ (b)(E)-pent-2-enal $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ (Z)-pent-2-en-1-ol** $22 \pm 1$ (b) $27 \pm 3$ (a) $18 \pm 1$ (b)pent-1-en-3-ol*** $8 \pm 2$ (b) $21 \pm 3$ (a) $17 \pm 1$ (a)terpinen-4-ol* $22 \pm 6$ (a) $14 \pm 5$ (a,b) $10 \pm 2$ (b)total:115321951988   | 2-methylbut-3-en-2-ol*      | 586 ± 74 (b)           | $1670 \pm 548$ (a)     | 1378 ± 197 (a,b)       |  |  |
| pent-1-en-3-one* $28 \pm 2$ (b) $57 \pm 10$ (a) $49 \pm 12$ (a,b)(R)-oct-1-en-3-ol*** $5 \pm 1$ (b) $68 \pm 16$ (a) $10 \pm 3$ (b)(E)-pent-2-enal $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ (Z)-pent-2-en-1-ol** $22 \pm 1$ (b) $27 \pm 3$ (a) $18 \pm 1$ (b)pent-1-en-3-ol*** $8 \pm 2$ (b) $21 \pm 3$ (a) $17 \pm 1$ (a)terpinen-4-ol* $22 \pm 6$ (a) $14 \pm 5$ (a,b) $10 \pm 2$ (b)total:115321951988   | 1,8-cineol                  | $453 \pm 97$           | $308 \pm 51$           | $484 \pm 80$           |  |  |
| $(R)$ -oct-1-en-3-ol*** $5 \pm 1$ (b) $68 \pm 16$ (a) $10 \pm 3$ (b) $(E)$ -pent-2-enal $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ $(Z)$ -pent-2-en-1-ol** $22 \pm 1$ (b) $27 \pm 3$ (a) $18 \pm 1$ (b)pent-1-en-3-ol*** $8 \pm 2$ (b) $21 \pm 3$ (a) $17 \pm 1$ (a)terpinen-4-ol* $22 \pm 6$ (a) $14 \pm 5$ (a,b) $10 \pm 2$ (b)total:115321951988  | pent-1-en-3-one*            | $28 \pm 2$ (b)         | $57 \pm 10$ (a)        | $49 \pm 12$ (a,b)      |  |  |
| (E)-pent-2-enal $29 \pm 3$ $30 \pm 7$ $22 \pm 3$ (Z)-pent-2-en-1-ol** $22 \pm 1(b)$ $27 \pm 3 (a)$ $18 \pm 1 (b)$ pent-1-en-3-ol*** $8 \pm 2 (b)$ $21 \pm 3 (a)$ $17 \pm 1 (a)$ terpinen-4-ol* $22 \pm 6 (a)$ $14 \pm 5 (a,b)$ $10 \pm 2 (b)$ total:115321951988sum total:   | (R)-oct-1-en-3-ol***        | $5 \pm 1$ (b)          | $68 \pm 16$ (a)        | $10 \pm 3$ (b)         |  |  |
| (Z)-pent-2-en-1-ol** $22 \pm 1(b)$ $27 \pm 3 (a)$ $18 \pm 1 (b)$ pent-1-en-3-ol*** $8 \pm 2 (b)$ $21 \pm 3 (a)$ $17 \pm 1 (a)$ terpinen-4-ol* $22 \pm 6 (a)$ $14 \pm 5 (a,b)$ $10 \pm 2 (b)$ total:115321951988sum total:124271667517776   | (E)-pent-2-enal             | $29 \pm 3$             | $30 \pm 7$             | $22 \pm 3$             |  |  |
| pent-1-en-3-ol*** $8 \pm 2$ (b) $21 \pm 3$ (a) $17 \pm 1$ (a)terpinen-4-ol* $22 \pm 6$ (a) $14 \pm 5$ (a,b) $10 \pm 2$ (b)total:115321951988sum total:124271667517776  | (Z)-pent-2-en-1-ol**        | $22 \pm 1(b)$          | $27 \pm 3$ (a)         | $18 \pm 1$ (b)         |  |  |
| terpinen-4-ol* $22 \pm 6$ (a) $14 \pm 5$ (a,b) $10 \pm 2$ (b)total:115321951988sum total:124271667517776   | pent-1-en-3-ol***           | $8 \pm 2$ (b)          | $21 \pm 3$ (a)         | $17 \pm 1$ (a)         |  |  |
| total:     1153     2195     1988       sum total:     12427     16675     17776   | terpinen-4-ol*              | $22 \pm 6$ (a)         | $14 \pm 5 (a,b)$       | $10 \pm 2$ (b)         |  |  |
| sum total: 12427 16675 17776   | total:                      | 1153                   | 2195                   | 1988                   |  |  |
|  | sum total:                  | 12427                  | 16675                  | 17776                  |  |  |

### Table 2. Concentrations of Major Volatiles Isolated by Means of VHS from Ripe Jostaberries Harvested at the Location Freising in Different Years<sup>a</sup>

"All compounds with concentrations  $\geq 20 \ \mu g/kg$  in at least one of the analyzed batches are considered. Correlation analysis was carried out by ANOVA. Levels of significance: p = 0-0.001: highly significant (\*\*\*), p = 0.001-0.01: very significant (\*\*), p = 0.01-0.05: significant (\*); statistically significant differences (Tukey's HSC) are indicated by different characters (a, b and c).

*n*-pentane (1:1; v:v). After drying with sodium sulfate, the extract was concentrated to 1 mL using a Vigreux column and to a final volume of 0.5 mL under a gentle nitrogen flow. All VHS-isolations were carried out in triplicate and the extracts were analyzed by HRGC-FID as well as by HRGC-MS.

**Capillary Gas Chromatography (HRGC-FID).** The separations were performed on a Carlo Erba Mega II 8575 series gas chromatograph (Thermo Fisher Scientific, Dreieich, Germany) equipped with a split/splitless injector (215 °C, split ratio 1:10), a flame ionization detector (FID) and a flame photometric detector (FPD) operating at 235 °C. The column used was a 60 m × 0.32 mm (i.d.) fused silica capillary column coated with DB-Wax (0.25  $\mu$ m film thickness; J&W Scientific). The oven temperature was programmed from 40 °C (5 min hold) at 4 °C/min to 240 °C (25 min hold). The carrier gas used was hydrogen at a constant inlet pressure of 110 kPa. Data acquisition was done via Chromcard software (Thermo Fisher Scientific). Retention indices were calculated on the basis of the analysis of *n*-alkanes (C<sub>8</sub>-C<sub>32</sub>) under the same conditions.

**Quantitation.** FID response factors were determined with solutions of authentic compounds relative to the internal standard (0.1  $\mu g/\mu L$  in diethyl ether). Recovery rates were determined in triplicate from aqueous solutions and buffer solutions (hydrochloric acid-sodium citrate buffer, pH 3.5) for acids, respectively (100  $\mu L$  stock solution (3 mg reference and 3 mg heptan-2-ol in 1 mL ethanol), were isolated from 1 L of water or buffer by means of VHS). Recovery rates were determined for main representatives of the different compound classes: methyl butanoate (63 ± 18%), ethyl butanoate (76 ± 8%),

methyl (E)-but-2-enoate (82  $\pm$  5%), ethyl (E)-but-2-enoate  $(87 \pm 3\%)$ , methyl hexanoate  $(76 \pm 6\%)$ , methyl benzoate  $(87 \pm$ 13%), (E)-hex-2-en-1-ol (77  $\pm$  7%), (Z)-hex-3-en-1-ol (76  $\pm$  5%), hexanol (82  $\pm$  2%), hexanal (86  $\pm$  4%), (E)-hex-2-enal (85  $\pm$  6%), (E)-hex-3-enal ( $29 \pm 7\%$ ), (Z)-hex-3-enal ( $30 \pm 10\%$ ), oct-1-en-3-ol  $(101 \pm 0\%)$ , 2-methylbut-3-en-2-ol (40  $\pm 15\%$ ), 1,8-cineol (86  $\pm$ 14%), terpinen-4-ol (83  $\pm$  8%), and acetophenone (92  $\pm$  4%). Recovery rates of acids, such as acetic acid, propanoic acid, butanoic acid, (E)-hex-2-enoic acid, (E)-hex-3-enoic acid, dimethylmalonic acid and cinnamic acid were less than 13%; therefore, members of this class of substances were not quantified. The limits of detection and the limits of quantitation were determined for octanal, (E)-oct-2-enal, ethyl hexanoate, methyl 3-hydroxybutanoate and pent-1-en-3-ol as representatives.<sup>10</sup> Four concentrations in the range from 625 to 6250 ng/mL were analyzed in triplicate, and by determining a calibration curve, the limits of detection and the limits of quantitation were calculated (assumption: recovery rate and response factor = 1).

**Gas Chromatography–Mass Spectrometry (GC–MS).** Mass spectral data were obtained on a gas chromatograph–mass spectrometer (GC  $8000^{\text{TOP}}$  with a Voyager GC–MS, Thermo Fisher Scientific) equipped with a split/splitless injector (220 °C, split ratio 1:50). The separation was performed on a 30 m × 0.25 mm (i.d.) fused silica capillary column coated with DB-WaxEtr (0.5  $\mu$ m film thickness; J&W Scientific). The oven temperature was programmed from 40 °C (5 min hold) at 4 °C/min to 240 °C (25 min hold). The carrier gas used was helium at a constant inlet pressure of 75 kPa. Ionization was set at 70 eV, source temperature at 200 °C, and interface temperature

#### Table 3. Concentrations of Volatiles in Underripe and Ripe Jostaberries<sup>a</sup>

|                              | underripe                   | ripe             |                           | underripe                   | ripe                        |
|------------------------------|-----------------------------|------------------|---------------------------|-----------------------------|-----------------------------|
| compounds                    | $\left[\mu g/kg\right]^{b}$ | $[\mu g/kg]^b$   | compounds                 | $\left[\mu g/kg\right]^{b}$ | $\left[\mu g/kg\right]^{b}$ |
| C <sub>6</sub> -compounds    |                             |                  | alcohols                  |                             |                             |
| (E)-hex-2-enal***            | $2133 \pm 1282$             | $13583 \pm 1393$ | (Z)-pent-2-en-1-ol        | $30 \pm 0$                  | $28 \pm 1$                  |
| ( <i>Z</i> )-hex-3-enal **   | $17891 \pm 2653$            | 6006 ± 852       | pent-1-en-3-ol            | $29 \pm 3$                  | $28 \pm 2$                  |
| hexanal***                   | $211 \pm 13$                | 486 ± 36         | 2-methylpropan-1-ol*      | n.q.                        | 9 ± 5                       |
| ( <i>E</i> )-hex-2-en-1-ol*  | $260 \pm 34$                | $381 \pm 31$     | (E)-pent-2-en-1-ol        | $4 \pm 0$                   | $4 \pm 0$                   |
| (E)-hex-3-enal**             | 621 ± 105                   | 318 ± 34         | ethan-1-ol                | n.d.                        | $4 \pm 3$                   |
| (Z)-hex-3-en-1-ol***         | $1042 \pm 112$              | $264 \pm 20$     | benzylalkohol             | n.d.                        | n.q.                        |
| (Z)-hex-2-enal               | $22 \pm 12$                 | 44 ± 10          | pentan-2-ol               | n.q.                        | n.d.                        |
| hexan-1-ol                   | $28 \pm 3$                  | $25 \pm 4$       | octan-1-ol**              | $14 \pm 4$                  | n.d.                        |
| ( <i>E</i> )-hex-3-en-1-ol** | $27 \pm 6$                  | $10 \pm 1$       | total                     | 319                         | 1116                        |
| total                        | 22237                       | 21117            | terpenes                  |                             |                             |
| esters                       |                             |                  | 1,8-cineol                | $342 \pm 269$               | 430 ± 7                     |
| methyl butanoate**           | 398 ± 92                    | $2019 \pm 527$   | terpinen-4-ol             | $8 \pm 1$                   | $7 \pm 1$                   |
| ethyl butanoate**            | 9 ± 5                       | $123 \pm 34$     | sabinene                  | 6 ± 2                       | $5 \pm 1$                   |
| methyl (E)-but-2-enoate***   | n.d. <sup>c</sup>           | $110 \pm 18$     | $\alpha$ -terpineol       | $2 \pm 2$                   | $3 \pm 0$                   |
| methyl benzoate**            | $15 \pm 2$                  | $109 \pm 23$     | $\beta$ -pinene           | $2 \pm 2$                   | n.d.                        |
| methyl hexanoate             | $10 \pm 9$                  | $28 \pm 9$       | terpinolene               | n.d.                        | n.q.                        |
| methyl octanoate             | $25 \pm 6$                  | $17 \pm 3$       | γ-terpinene               | n.q.                        | n.d.                        |
| ethyl decanoate***           | n.d.                        | $10 \pm 2$       | total                     | 378                         | 454                         |
| methyl decanoate***          | n.d.                        | $9 \pm 2$        | ketones                   |                             |                             |
| benzyl acetate***            | n.d.                        | $7 \pm 0$        | pent-1-en-3-one           | 64 ± 4                      | 69 ± 13                     |
| ethyl (E)-but-2-enoate***    | n.d.                        | $7 \pm 1$        | oct-1-en-3-one*           | $20 \pm 9$                  | n.d.                        |
| methyl salicylate            | $4 \pm 1$                   | $5 \pm 1$        | total                     | 84                          | 69                          |
| (E)-hex-2-enyl acetate       | $4 \pm 3$                   | $3 \pm 3$        | aldehydes                 |                             |                             |
| hexyl acetate                | n.q. <sup>d</sup>           | n.q.             | (E)-pent-2-enal           | $31 \pm 5$                  | $27 \pm 5$                  |
| ethyl hexanoate              | n.d.                        | n.q.             | nonanal**                 | $5 \pm 2$                   | n.q.                        |
| 3-methylbut-2-enyl acetate   | n.q.                        | n.d.             | (Z)-pent-2-enal***        | $21 \pm 1$                  | n.d.                        |
| total                        | 466                         | 2447             | total                     | 38                          | 27                          |
|                              |                             |                  | others                    |                             |                             |
| alcohols                     |                             |                  | C5-compounds <sup>e</sup> | $12 \pm 2$                  | $10 \pm 2$                  |
| 2-methylbut-3-en-2-ol**      | $94 \pm 23$                 | $1011 \pm 328$   | heptadienal isomer        | $6 \pm 0$                   | $6 \pm 1$                   |
| (R)-oct-1-en-3-ol*           | 148 ± 47                    | $32 \pm 7$       | total                     | 18                          | 16                          |

"Data relate to material from Deutenkofen; underripe and ripe berries were harvested on the same day: 02 July, 2012. Correlation analysis was carried out by ANOVA. Levels of significance: p = 0-0.001: highly significant (\*\*\*), p = 0.001-0.01: very significant (\*\*), p = 0.01-0.05: significant (\*) <sup>b</sup>Triplicate analysis of underripe and ripe fruits: mean  $\pm$  standard deviation. 'Not detectable: concentration below limit of identification (0.6  $\mu$ g/kg). <sup>d</sup>Not quantifiable: concentration below limit of quantitation (1.7  $\mu$ g/kg). <sup>e</sup>Coelution of propyl acetate, pentan-2-one, pentan-3-one and pentanal.

at 240 °C. Data acquisition was done via Xcalibur software, version 1.4 (Thermo Fisher Scientific).

**Gas Chromatography-Olfactometry.** The GC-system consisted of a Carlo Erba Strumentazione 4200 gas chromatograph equipped with a FID (230 °C) and a sniffing port (230 °C), using a deactivated capillary column (30 cm) and a split/splitless injector (220 °C, split ratio 1:10). Volatiles were separated on a 60 m × 0.32 mm (i.d.) fused silica capillary column (injection volume 1  $\mu$ L) coated with DB-Wax (0.25  $\mu$ m film thickness; J&W Scientific). The oven temperature was programmed from 55 °C (10 min hold) at 4°/min to 240 °C (25 min hold). The carrier gas used was hydrogen at a constant inlet pressure of 110 kPa. The GC-effluent was split 1:1 among FID and sniffing port; no humidified air or nitrogen was used.

**Statistical Analysis.** XLSTAT (Addinsoft, Version 2008.4.01) was used for statistical tests (confidence interval for all tests: 95%). Correlation analyses were carried out with ANOVA. Levels of significance: p = 0-0.001: highly significant (\*\*\*), p = 0.001-0.01: very significant (\*\*\*), p = 0.01-0.05: significant (\*). Statistically significant differences were identified by Tukey's HSC.

Aroma Extract Dilution Analysis (AEDA). Three extracts ( $500 \ \mu L$  each) obtained by VHS from ripe jostaberries (date of harvest: 30 June, 2011; location: Oberrotweil) were combined and gently concentrated to 0.5 mL under nitrogen flow. The concentrated extract was diluted gradually with the solvent mixture of diethyl ether and

*n*-pentane (v:v; 1:1) and analyzed by GC-O until no odor was detectable anymore. AEDA was done by one panelist by sniffing of the whole chromatogram (in triplicate for the concentrated extract and once for the subsequent dilutions); at the higher dilution steps, the sensorial assessment was limited to the odor-active areas remaining in the chromatogram.

**Determination of Odor Thresholds.** Odor thresholds were determined by a panel (at least 10 participants) in a triangle-test using the "forced choice" technique. The compounds were dissolved in water and the solutions were assessed in glasses covered with lids.

**Reconstitution Experiments.** Reconstitution models were prepared based on the concentrations of aroma-active compounds determined in the batch of fresh jostaberries from the location Oberrotweil (30 June, 2011), extracts of which have been used for AEDA: (*Z*)-hex-3-anal (955  $\mu$ g/kg), 1,8-cineol (447  $\mu$ g/kg), ethyl butanoate (712  $\mu$ g/kg), (*E*)-hex-2-enal ( $\mu$ g/kg), hexanal (134  $\mu$ g/kg), pent-1-en-3-one (18  $\mu$ g/kg), methyl butanoate (2725  $\mu$ g/kg), ethyl hexanoate (10  $\mu$ g/kg), (*E*)-hex-3-enal (116  $\mu$ g/kg) and oct-1-en-3-one (0.01  $\mu$ g/kg). Appropriate amounts of stock solutions of the odorants were dissolved using an aqueous solution of oxalic acid (40 mg/L), malic acid (3.5 g/L), ascorbic acid (1.5 g/L), citric acid (25 g/L), glucose (30 g/L), fructose (35 g/L) and sucrose (20 g/L).

**Aroma Profile Tests.** Samples (15 mL) were placed into glasses with lids and were orthonasally evaluated by a sensory panel of at least

|                                     |                   |                           |                        | threshold       |        |   |                  |
|-------------------------------------|-------------------|---------------------------|------------------------|-----------------|--------|---|------------------|
| odorant                             | $\mathrm{RI}^{a}$ | odor quality <sup>b</sup> | FD factor <sup>c</sup> | [µg/L in water] | remark | $\left[\mu \mathrm{g}/\mathrm{kg}\right]^d$ | OAV <sup>e</sup> |
| (Z)-hex-3-enal                      | 1138              | grassy                    | 32                     | 0.6             | f      | 1476  | 2460             |
| 1,8-cineol                          | 1200              | eucalyptus                | 512                    | 2               | f      | 499   | 250              |
| ethyl butanoate                     | 1034              | pineapple-like            | 4096                   | 2.5             | f      | 539   | 216              |
| (E)-hex-2-enal                      | 1211              | apple-like                | 32                     | 77              | f      | 8139  | 106              |
| hexanal                             | 1075              | fatty-green               | 256                    | 4               | f      | 230   | 58               |
| pent-1-en-3-one                     | 1009              | musty, pungent            | 16                     | 1               | f      | 45  | 45               |
| methyl butanoate                    | 975               | fruity, cheesy            | 128                    | 63              | f      | 2526  | 40               |
| ethyl hexanaote                     | 1232              | green, fruity             | 32                     | 1.4             | f      | 8   | 6                |
| (E)-hex-3-enal                      | 1133              | green                     | 32                     | 160             | g      | 206   | 1                |
| nonanal                             | 1391              | waxy                      | 16                     | 1               | h      | n.q. <sup><i>i</i></sup>                    |                  |
| 3-methylbut-2-enyl acetate          | 1251              | musty, green              | 64                     |                 |        | 2   |                  |
| (Z)-octa-1,5-dien-3-ol <sup>j</sup> | 1490              | mushroom-like             | 256                    | 0.1             | k      | n.d. <sup>1</sup>                           |                  |
| propan-2-thiol                      | 801               | sulfurous                 | 64                     | 0.001           | т      | n.d.  |                  |
| oct-1-en-3-one                      | 1296              | mushroom-like             | 64                     | 0.005           | n      | n.d.  |                  |
| ethyl acetate                       | 886               | fruity                    | 32                     | 5               | 0      | n.c. <sup>p</sup>                           |                  |
| methyl (E)-but-2-enoate             | 1096              | fruity, pungent           | 2048                   | 124             | f      | 117   | <1               |
| (E)-pent-2-enal                     | 1120              | green, pungent            | 128                    | 1500            | 9      | 27  | <1               |
| hexan-1-ol                          | 1355              | pungent, green            | 1024                   | 500             | r      | 75  | <1               |
| (E)-hex-3-en-1-ol                   | 1364              | geranium-like             | 64                     | 1000            | \$     | 39  | <1               |
| 2-methylpropanoic acid              | 1562              | musty                     | 64                     | 10              | t      | n.q.  | <1               |
| linalyl acetate                     | 1552              | sweet, herbal             | 32                     | 24              | f      | n.q.  | <1               |
| 2-methylpropyl acetate              | 968               | green, fresh              | 16                     | 441             | и      | n.q.  | <1               |
| 2-methylpropan-1-ol                 | 1084              | cheesy, alcoholic         | 16                     | 75000           | \$     | 27  | <1               |
| (E)-linalool oxide                  | 1428              | earthy, musty             | 16                     | 100             | ν      | n.q.  | <1               |

<sup>*a*</sup>linear retention indices on a DB-Wax-column (see Materials and Methods). <sup>*b*</sup>assessed at AEDA. <sup>*c*</sup>GC-O and AEDA were performed by one panelist using a concentrated VHS extract corresponding to 1.5 kg of jostaberries obtained from Oberrotweil on 30 June, 2011. <sup>*d*</sup>Concentrations calculated from 9 batches of ripe jostaberries (listed in Materials and Methods). <sup>*e*</sup>Odor activity value, calculated by division of individual, averaged concentration and odor threshold. <sup>*f*</sup>Determined in triangle test. <sup>*g*</sup>Reference 36. <sup>*h*</sup>Reference 37. <sup>*i*</sup>Not quantifiable: concentration below limit of quantitation (1.7  $\mu$ g/kg). <sup>*j*</sup>Identification by comparison of mass spectrum and odor description with literature<sup>25</sup> and by comparison of the linear retention index using a mushroom extract (linolenic acid added at homogenization analogous to ref 25) and literature data.<sup>38 k</sup>Reference 39. <sup>*l*</sup>not detectable: concentration below limit of detection (0.6  $\mu$ g/kg). <sup>*m*</sup>Reference 40. <sup>*n*</sup>Reference 41. <sup>*o*</sup>Reference 42. <sup>*p*</sup>Not calculable: recovery too poor (see Materials and Methods). <sup>*q*</sup>Reference 43. <sup>*k*</sup>Reference 44. <sup>*k*</sup>Reference 45. <sup>*k*</sup>Reference 48.

10 assessors. Descriptors used were determined in preliminary evaluations on the basis of the odor properties of reference compounds dissolved in water at concentrations 100 times above their odor thresholds. The following combinations of reference odorants and odor descriptions (given in parentheses) were used: ethyl butanoate (pineapple-like), methyl benzoate (sweet), (*E*)-hex-2-enal (apple-like), (*Z*)-hex-3-enal (grassy), hexanal (fatty-green), 1,8-cineol (eucalyptuslike), acetic acid (sour) and pent-1-en-3-one (musty-pungent). Assessors were asked to rate each descriptor in the samples presented on a seven point scale from 0 (not detectable) to 3 (strong). The sensory evaluation of the jostaberries was performed with the cut fruit within 30 s. For each descriptor, a new, intact berry was used.

#### RESULTS AND DISCUSSION

Analysis of the Volatile Profile of Jostaberries. Volatile constituents of jostaberries were isolated via vacuum headspace extraction (VHS). This gentle method allows the isolation of volatiles without thermal treatment, has proven to be suitable for generating extracts exhibiting the aroma of fresh fruits and has recently been employed to isolate the volatiles from gooseberries.<sup>11–14</sup> The volatile compounds identified and quantified in VHS-extracts from jostaberries by means of HRGC-FID and HRGC-MS are presented in Table 1. C<sub>6</sub>-components and esters turned out to be the major compound classes. C<sub>6</sub>-components represent secondary flavor compounds, formed enzymatically from linoleic and linolenic acid, respectively, after disruption of the cell structure. They are important for plants

defense strategies and pest resistance and are widely used as flavoring substances because of their fresh, green odors.<sup>15,16</sup> The main  $C_6$ -constituent was identified as (*E*)-hex-2-enal, known as quantitatively dominating  $C_6$ -compound in other fruits, such as kiwis and nectarines.<sup>17,18</sup> In jostaberries the corresponding alcohol (E)-hex-2-en-1-ol as well as the positional isomers (Z)-hex-3-enal and (Z)-hex-3-en-1-ol were also detected in fairly high concentrations. The ester profile of jostaberries is mainly characterized by short-chain methyl and ethyl esters. Methyl butanoate constituting up to 87% of the total esters and up to 27% of the total volatiles, represents by far the main ester. In addition to C<sub>6</sub>-compounds and esters, 1,8-cineol and 2methylbut-3-en-2-ol are also present at high concentrations. 1,8-Cineol, also known as eucalyptol, accounts for up to 89% of the essential oil of *Eucalytus globulus*.<sup>19</sup> Due to its characteristic fresh, camphor-like odor, there are numerous applications for the flavoring of foods, beverages, cosmetics and in the fragrance industry.<sup>19,20</sup> 2-Methylbut-3-en-2-ol is known as a volatile compound of the creosotebush as well as of honey and matsutakemushrooms.<sup>21–23</sup>

Impact Factors on the Volatile Composition of Jostaberries. The data in Table 1 represent the concentrations of volatile constituents in ripe jostaberries, all harvested at the ripe state at three locations in Southern Germany in 2011. Although the geographical distances are relatively small (at most 260 km), the data indicate that for the selected growing sites

the factor location has only a minor impact on the volatile composition. Except for variations observed for individual substances, for example, methyl and ethyl butanoate or (R)-oct-1en-3-ol, the quantitative distributions of most constituents and of the compound classes are quite comparable. It is noteworthy that in all three batches at least 91% of the total volatiles are represented by only eight components: (E)-hex-2-enal, (E)hex-2-en-1-ol, (Z)-hex-3-enal, (Z)-hex-3-en-1-ol, methyl butanoate, ethyl butanoate, 2-methylbut-3-en-2-ol and 1,8-cineol.

In addition, ripe jostaberries harvested at the same location (Freising) in different years were investigated (Table 2). The total amounts of volatiles, the distributions of compound classes and the contents of most constituents were quite comparable in 2011 and 2012. The material harvested in 2010 exhibited a profile of  $C_6$ -compounds similar to those of 2011 and 2012; however, the contents of methyl and ethyl butanoate and of 2-methylbut-3-en-2-ol were significantly lower.

Finally, the impact of the state of ripeness was assessed by investigating not only ripe but also underripe jostaberries (Table 3). The total of C<sub>6</sub>-compounds remained nearly constant, but the distribution of single compounds changed considerably. While the  $C_6$ -profile of underripe jostaberries is dominated by (Z)hex-3-enal, ripe jostaberries are characterized by (E)-hex-2-enal as the main component. Also, the concentrations of (E)-hex-3enal and (Z)-hex-3-en-1-ol, being generated via isomerization and reduction from (Z)-hex-3-enal, decreased during the ripening process, whereas (E)-hex-2-en-1-ol was more abundant in ripe jostaberries. In addition, the concentration of hexanal, an oxidation product of linoleic acid, increased during the ripening process of the fruit. The most obvious changes during the ripening process were observed for the totals of esters (from 466 to 2447  $\mu$ g/kg) and alcohols (from 319 to 1116  $\mu$ g/kg). The increase of esters was caused by rising concentrations of almost every ester-compound, but most clearly for methyl butanoate (from 398 to 2019  $\mu$ g/kg). The alcohols showed different trends: the concentrations of (Z)-/(E)-pent-2-en-1-ol and pent-1-en-3-ol remained constant, whereas the contents of (R)-oct-1-en-3-ol and octan-1-ol decreased and those of 2-methylbut-3-en-2-ol and 2-methylpropan-1-ol increased significantly. 2-Methylbut-3-en-2-ol emitted from pine needles has been shown to be biosynthesized enzymatically from dimethylallyl diphosphate.<sup>24</sup> Next to the decreasing amount of (R)-oct-1-en-3-ol also the concentration of oct-1-en-3-one declined during the ripening-process. Both compounds are generated enzymatically from unsaturated fatty acids and are characterized by a mushroom-like odor.<sup>25,26</sup>

Screening of the Sensory Contributions of Aroma Compounds. The extracts obtained by VHS were reminiscent of fresh jostaberries and exhibited fresh, green as well as black currant-like odor notes. A pooled and concentrated extract of 1.5 kg jostaberries was used for AEDA. A total of 58 odor-active compounds were detected; those with flavor dilution factors (FD)  $\geq$  16 are listed in Table 4. Particularly, lipid oxidation products and short chain esters turned out to be among the potent odorants. As a second step the odor activity values (OAV), that is, the ratios of concentrations and odor thresholds of the individual substances, were calculated. Considering that odor thresholds cited in literature vary strongly, odor thresholds for substances with a great impact on the aroma of jostaberries, as indicated by the FD-factors, were determined by an own panel. (Z)-Hex-3-enal had by far the greatest impact on the aroma of jostaberries, followed by 1,8-cineol and ethyl butanoate. For a total of nine compounds OAVs  $\geq$  1 could be

calculated; these were used as basis for the subsequent recombination experiments. Considering the low odor threshold of oct-1-en-3-one (0.005  $\mu$ g/L) and of the structurally related (*Z*)octa-1,5-dien-3-ol (0.1  $\mu$ g/L), the contribution of a mushroomnote to the overall flavor of jostaberries seemed probable; therefore, oct-1-en-3-one was also included in the model. Since its concentration in the investigated ripe jostaberries was below the limits of detection and quantitation, respectively, an amount corresponding to twice the odor threshold concentration was used. In order to imitate a berry-like matrix, recombinates were prepared in an aqueous solution of sugars and organic acids, naturally contained in the berries. According to the panelists the recombinate was reminiscent of jostaberry, combining a mild black currant note with a green gooseberry-like aroma. The aroma profile was in good agreement with that of fresh jostaberries (Figure 1).



Figure 1. Comparison of the aroma profiles of the jostaberry reconstitution model (continuous line) and the original fruit (broken line).

**Comparison of Major Volatiles of Jostaberries, Gooseberries and Black Currants.** Considering that jostaberry is a hybrid of black currant and gooseberry, it seemed reasonable to have a preliminary screening of the contribution of the pools of volatiles in these starting materials to those present in jostaberries. As a first attempt, the eight compounds shown to constitute at least 91% of the total volatiles in the

 Table 5. Concentrations of Main Volatiles in Jostaberries

 Compared to Those in Gooseberries and Black Currants

|                          | jostaberries <sup>a</sup> | gooseberries <sup>b</sup> | black currants <sup>c</sup> |
|--------------------------|---------------------------|---------------------------|-----------------------------|
|                          | $[\mu g/kg]^d$            | $[\mu g/kg]^d$            | $[\mu g/kg]^d$              |
| $C_6$ -components        |                           |                           |                             |
| (E)-hex-2-enal           | 9613 ± 819                | $509 \pm 157$             | $2227 \pm 404$              |
| (Z)-hex-3-enal           | $565 \pm 226$             | $1128 \pm 81$             | 461 ± 99                    |
| (E)-hex-2-en-1-ol        | $525 \pm 180$             | 66 ± 8                    | $257 \pm 1$                 |
| (Z)-hex-3-en-1-ol        | 186 ± 11                  | $71 \pm 11$               | $152 \pm 35$                |
| hemi-/ monoterpene alcol | iols                      |                           |                             |
| 2-methylbut-3-en-2-ol    | $1670 \pm 548$            | n.d. <sup>e</sup>         | $238 \pm 124$               |
| 1,8-cineol               | $308 \pm 51$              | n.d.                      | $71 \pm 20$                 |
| esters                   |                           |                           |                             |
| methyl butanoate         | $2330 \pm 291$            | $1276 \pm 137$            | $1774 \pm 1090$             |
| ethyl butanoate          | 348 ± 66                  | 47 ± 35                   | $1773 \pm 1523$             |
|                          |                           |                           |                             |

<sup>*a*</sup>Harvested on 13 July, 2011 in Freising. <sup>*b*</sup>Data correlate to gooseberries var. Achilles (25 August, 2010).<sup>14</sup> <sup>*c*</sup>Obtained from a local market on 20 June, 2011. <sup>*d*</sup>Data from triplicate experiments for each batch: mean  $\pm$  standard deviation. <sup>*e*</sup>Not detectable: concentration below limit of identification (0.6  $\mu$ g/kg).

batches of gooseberries analyzed in this study were selected for comparison (Table 5). The literature data available on the volatile profiles of black currants refer to frozen fruits.<sup>27–33</sup> Taking into account the known influence of freezing on the generation of C<sub>6</sub>-components, these data were not considered suitable as basis for a comparison. Therefore, volatiles were isolated from a batch of fresh black currants via VHS in the same way as performed for jostaberries and gooseberries.<sup>14</sup> For gooseberries, a batch of var. Achilles, exhibiting a spectrum of volatiles close to the mean distribution determined in this fruit, was selected for comparison.<sup>14</sup>

As shown in Table 5, the  $C_6$ -profile of jostaberries exhibits characteristics similar to those of black currants: (E)-hex-2-enal represents the main  $C_6$ -component, followed by (E)-hex-2-en-1-ol and (Z)-hex-3-enal. The prominent role observed for (Z)hex-3-enal in the spectrum of C<sub>6</sub>-components in gooseberries is not reflected in jostaberries. 2-Methylbut-3-en-2-ol and 1,8cineol are examples of volatiles being highly abundant in jostaberries but not detected in the investigated gooseberries.14 Apparently, the genetic information for biosynthesis of these compounds in jostaberry exclusively stems from black currant. On the other hand, the pronounced preponderance of methyl butanoate compared to ethyl butanoate observed in gooseberries is also reflected in jostaberries, whereas in the investigated batches of black currants the concentrations were almost identical. Of course, these comparisons have to be considered preliminary and would have to be extended for a broader spectrum of constituents and fruit batches.

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#### Notes

The authors declare no competing financial interest.

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