**Supplementary file of the manuscript**

# Exploitation of virgin olive oil by-products (*Olea europaea* L.): phenolic and volatile compounds transformations phenomena in fresh two-phase olive pomace ("alperujo") under different storage conditions

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**Scheme S1.** Process diagram of the experimental plan

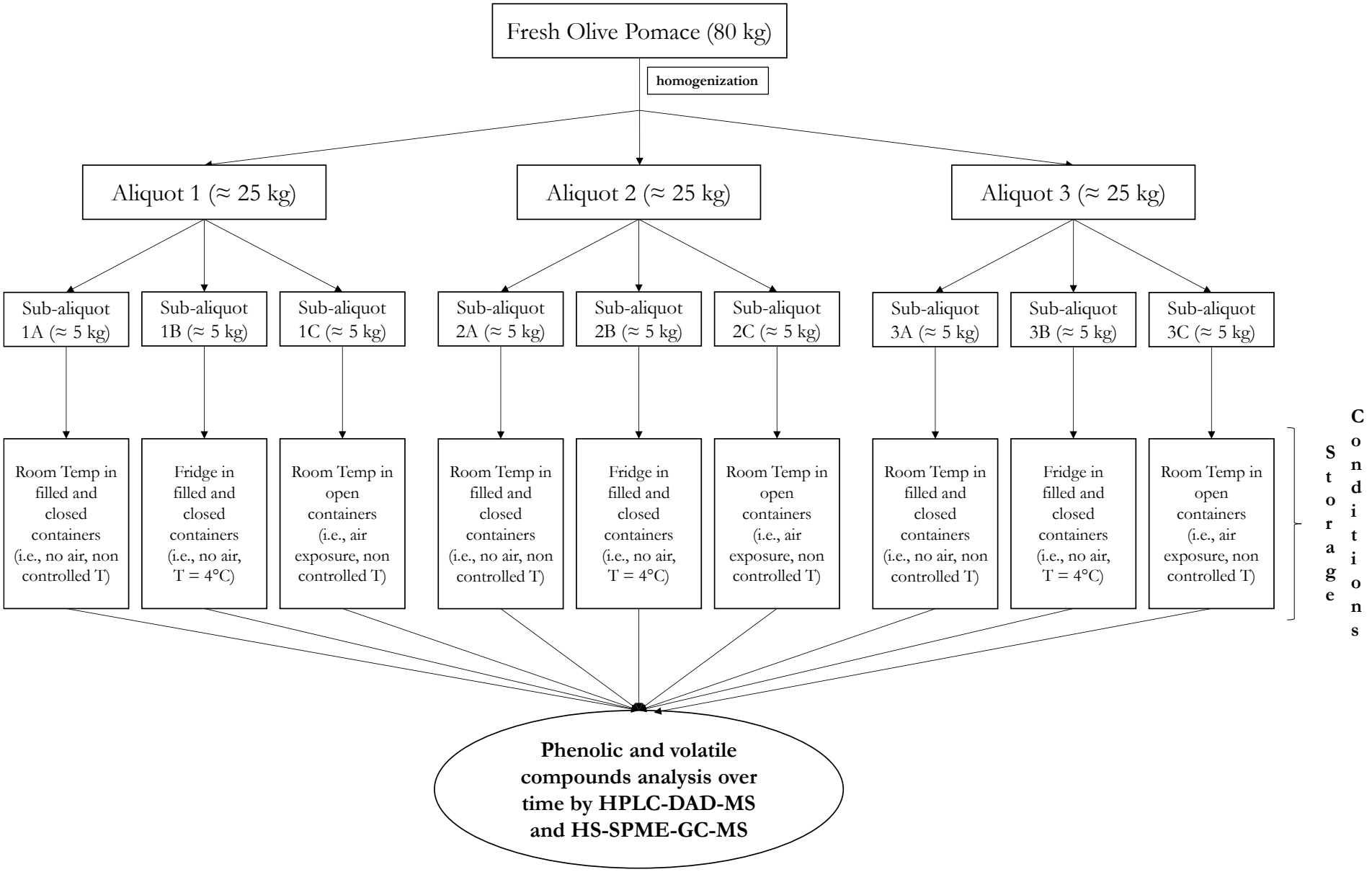
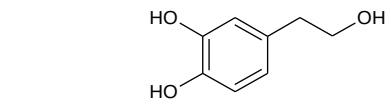
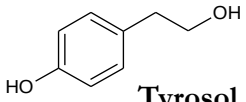


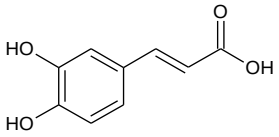
**Figure S1.** Chemical structure of the main phenolic compounds detected in alperujo samples.



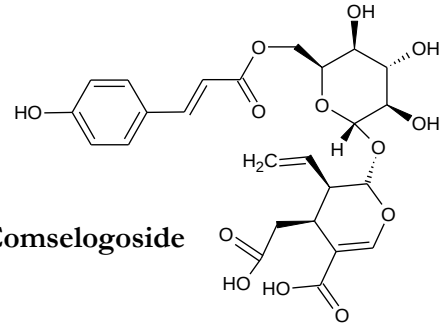
**Hydroxytyrosol**



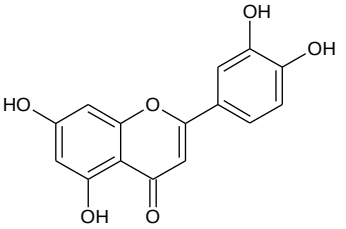
**Tyrosol**



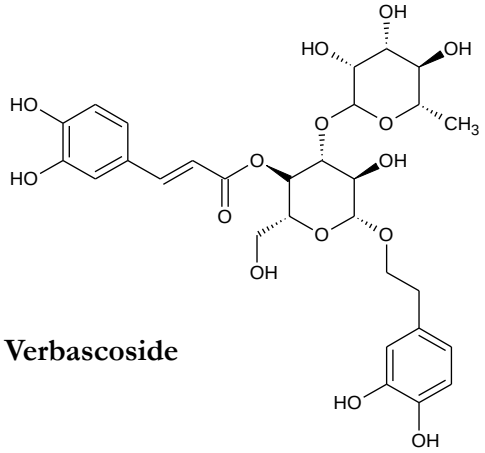
**Caffeic acid**



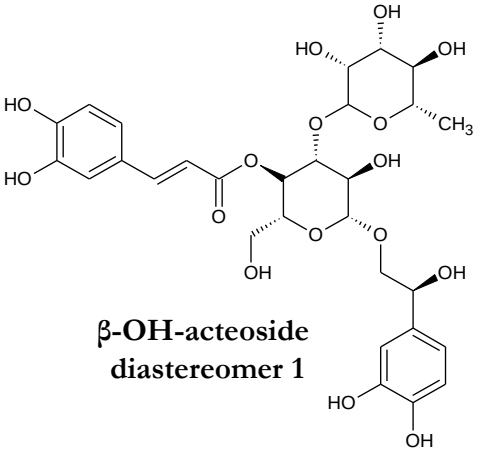
**Comselogoside**



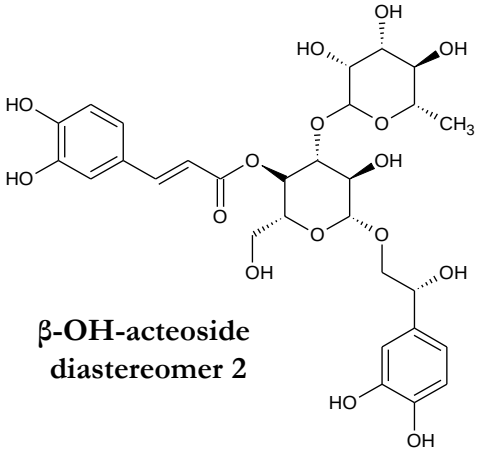
**Luteolin**



**Verbascoside**

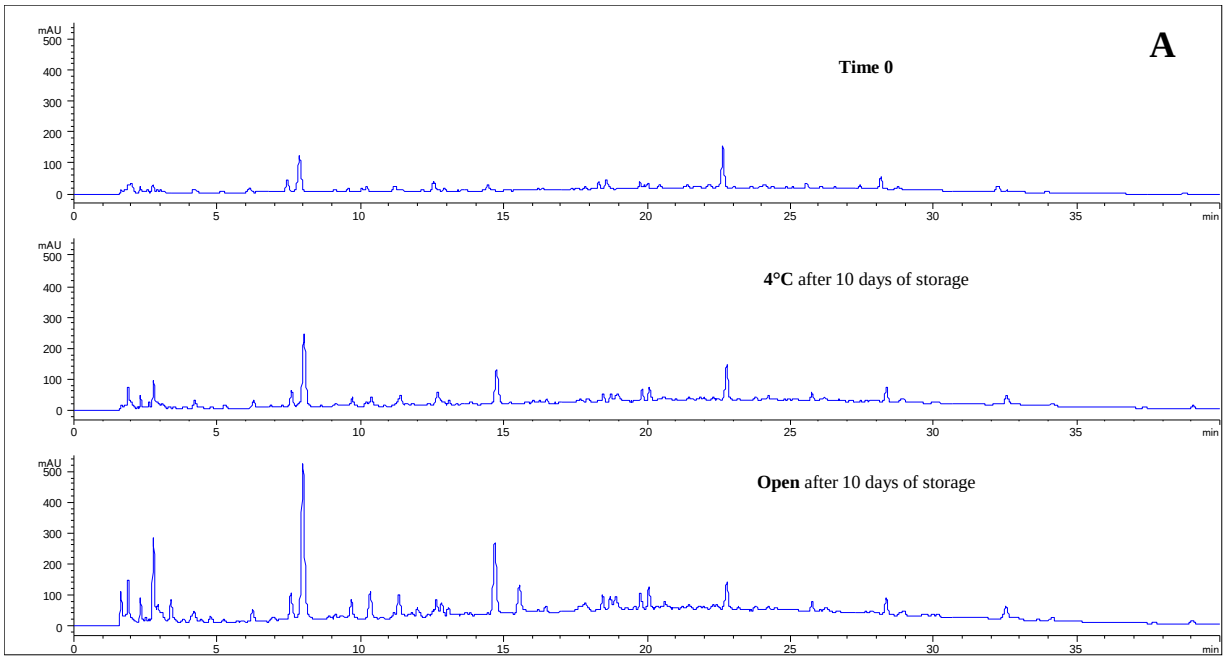


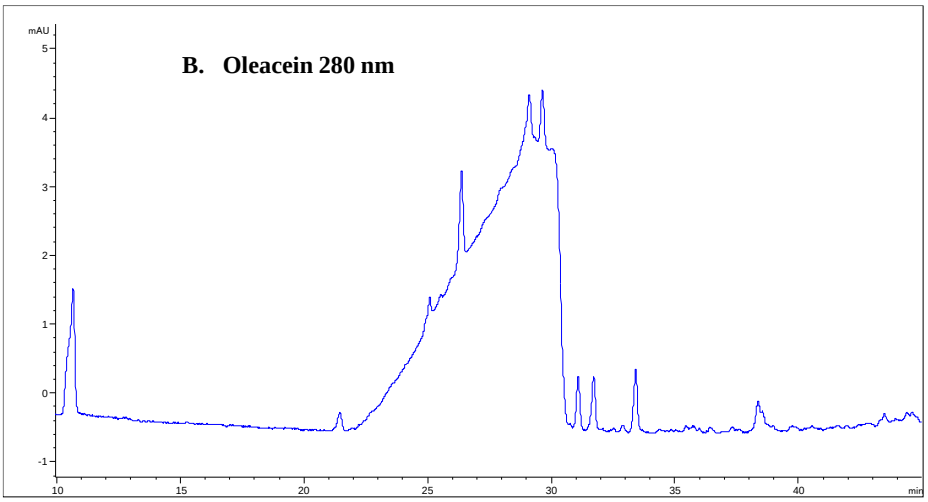
**β-OH-acteoside diastereomer 1**



**β-OH-acteoside diastereomer 2**

**Figure S2.** Chromatographic profile at 280 nm of A) the fresh alperujo sample at time 0 and after 10 days in open and 4°C conditions, B) the commercial standard of the dialdehydic form of decarboxymethyl oleuropein aglycone (oleacein), C) the commercial standard of the dialdehydic form of decarboxymethyl ligstroside aglycone (oleocanthal).



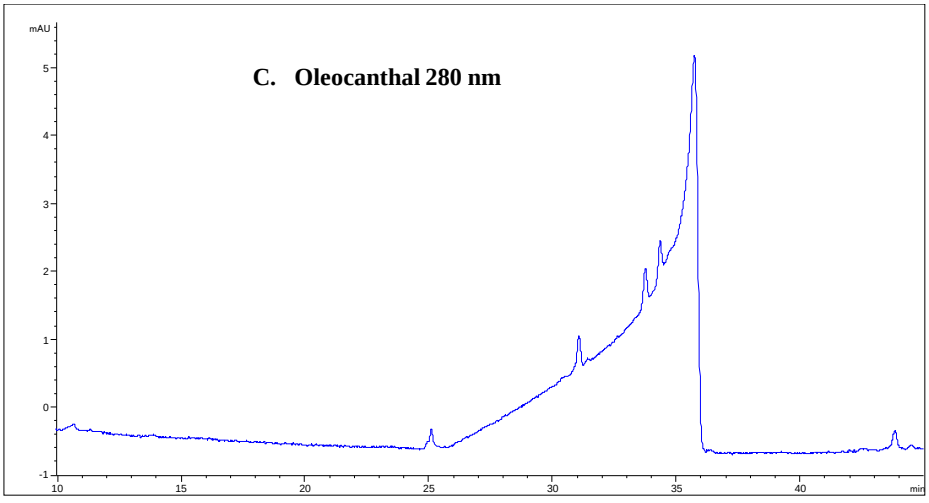



**Figure S3.** Total Ion Current (TIC) chromatograms of the volatile profile of the olive pomace at time 0 (A) and after storage in open containers after 2 days (B) and after 10 days (C). All the three chromatograms are reported at the same scale.

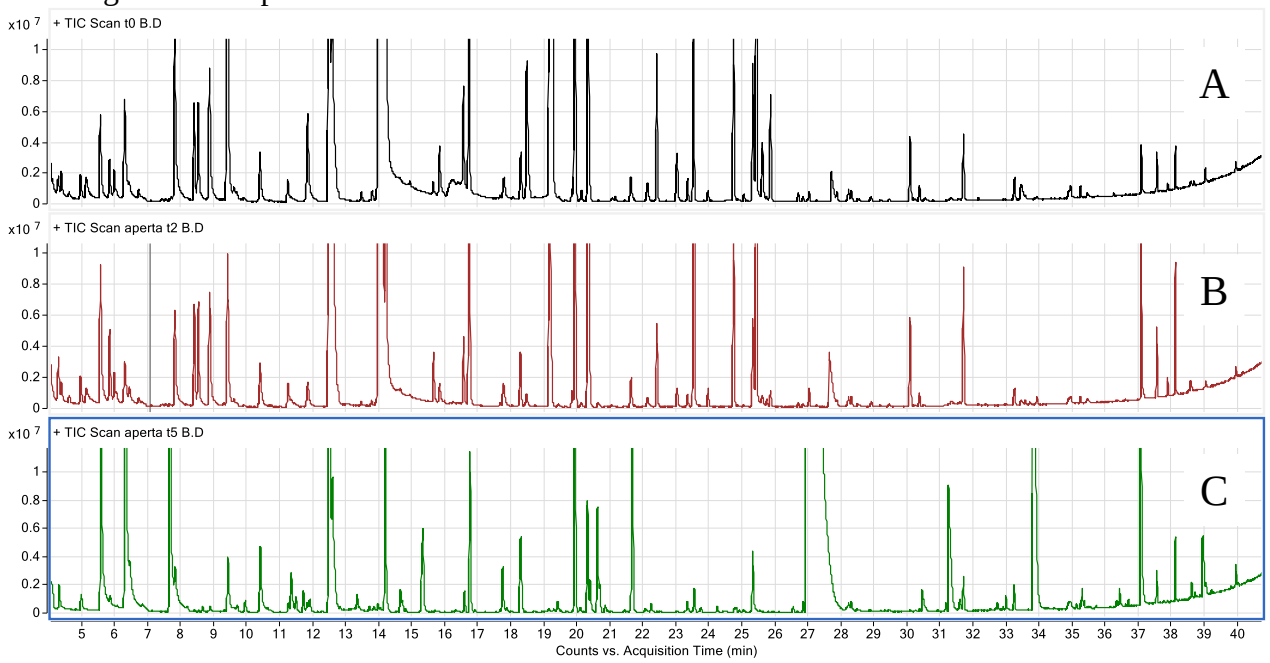


**Figure S4.** Evolution over storage of octane and styrene according to type of storage: at 4°C in the fridge (4°C), at room temperature in full close containers (close) and at room temperature in open containers. Data are the mean of 3 independent measurements and are expressed on dried weight basis.

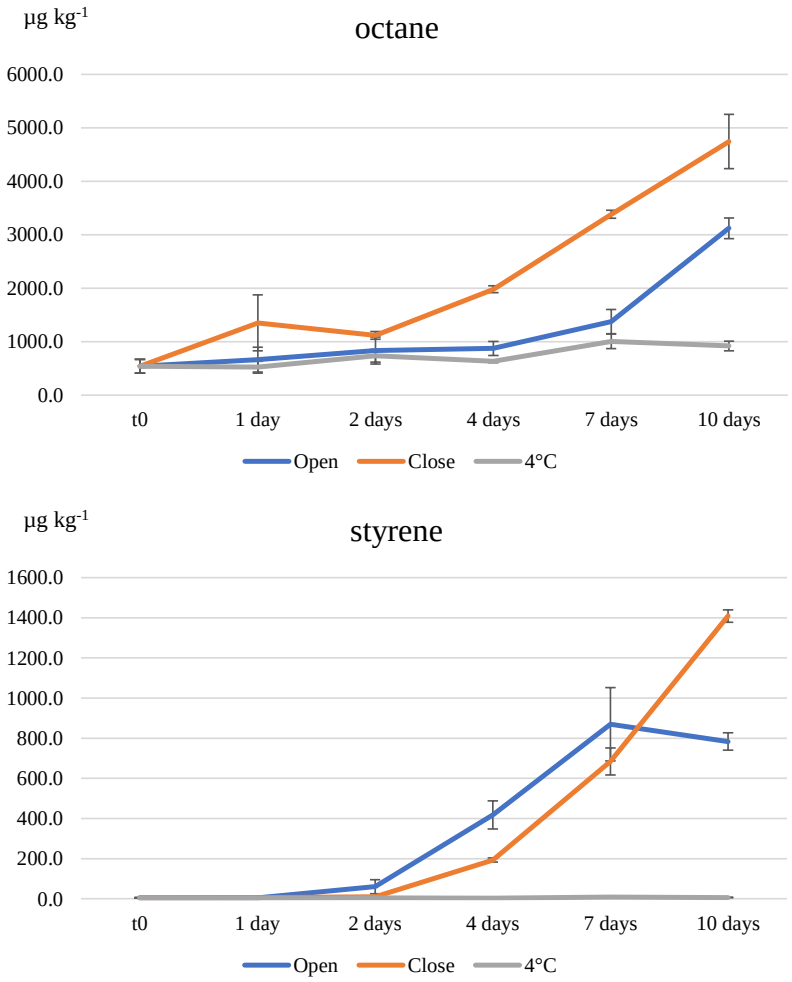


**Table S1**. *p*-values evaluated by two factor ANOVA for each phenolic molecule. The two factors were the type of storage (Storage) and storage time (Time), and the two-way interaction Storage × Time was also considered. Significant values at $p < 0.05$ are in italic

| | Storage | Time | Storage x Time |
|---|---|---|---|
| hydroxytyrosol glucoside | *8.4E-13* | *1.9E-13* | *7.4E-09* |
| hydroxytyrosol | *1.2E-11* | *8.9E-18* | *2.3E-14* |
| hydroxytyrosol after hydrolysis | *1.3E-06* | 0.18 | *1.9E-06* |
| tyrosol glucoside | *5.5E-09* | *3.4E-10* | *3.1E-07* |
| tyrosol after hydrolysis | *2.1E-04* | *4.3E-05* | *9.0E-06* |
| tyrosol | *3.2E-13* | *1.3E-18* | *1.8E-12* |
| caffeic acid | *4.4E-20* | *4.3E-31* | *1.6E-16* |
| β-OH-acteoside 1 | *2.7E-11* | *1.4E-17* | *2.8E-06* |
| β-OH-acteoside 2 | *1.9E-07* | *2.8E-15* | *2.2E-04* |
| verbascoside | *7.6E-14* | *1.1E-24* | *7.0E-11* |
| comselogoside | *1.5E-12* | *2.8E-20* | *2.7E-08* |
| luteolin | 0.43 | *3.7E-14* | *3.4E-05* |
| TPC | *5.1E-05* | *2.3E-05* | *1.3E-05* |

**Table S2.** VOCs data processing of alperujo samples. *p*-values calculated for each VOC by two factor ANOVA, where the two factors were the storage time (**time**) and the type of storage (**storage**). The two-way interaction time×storage is also reported. Non-significant values ($p > 0.05$) are in italic.

| | Storage | Time | Storage x Time |
|---|---|---|---|
| **Acetic acid** | 2.87333E-38 | 3.72917E-41 | 5.62416E-41 |
| **3-Methyl butanoic acid** | 2.52404E-34 | 2.86583E-38 | 1.80117E-40 |
| **(*E*)-2-Pentenoic acid** | 2.60434E-31 | 2.0849E-34 | 4.59378E-37 |
| **Pentanoic acid** | 2.66132E-30 | 2.73578E-33 | 1.66388E-34 |
| **Propanoic acid** | 1.22328E-28 | 1.73116E-30 | 1.56937E-32 |
| **Methyl 3-methylbutanoate** | 2.03372E-25 | 1.79038E-30 | 8.82867E-33 |
| **2-Methyl propanoic acid** | 4.98891E-28 | 2.96907E-30 | 1.56048E-32 |
| **Acetoin acetate** | 2.18257E-24 | 2.00839E-28 | 1.07438E-31 |
| **2-Methyl butanoic acid** | 1.06836E-23 | 4.96913E-28 | 1.50919E-29 |
| **3-Pentanol** | 1.87933E-22 | 2.25974E-27 | 1.1635E-29 |
| **1-Octen-3-ol** | 5.82112E-24 | 3.10772E-27 | 1.87237E-29 |
| **Methyl acetate** | 1.86333E-21 | 5.24335E-27 | 7.71643E-27 |
| **(*E*)-3-Hexenoic acid** | 1.2207E-21 | 1.98607E-25 | 2.57614E-26 |
| **2-methyl-1-butanol+3-methyl-1-butanol** | 2.9211E-22 | 8.98558E-25 | 2.64265E-24 |
| **4-Hepten-1-ol** | 4.23567E-28 | 6.30893E-24 | 1.40723E-26 |
| **Ethyl benzoate** | 1.07885E-21 | 2.35976E-23 | 2.34736E-25 |
| **1-Octen-3-one** | 1.79422E-20 | 2.93569E-23 | 4.40336E-24 |
| **Ethyl hexanoate** | 9.62267E-21 | 1.45063E-22 | 1.04466E-24 |
| **Ethyl-(*Z*)-3-hexenoate** | 4.64807E-16 | 1.23234E-21 | 9.5398E-26 |
| **Methyl hexanoate** | 5.17013E-11 | 2.0117E-21 | 3.27154E-10 |
| **Hexanoic acid** | 1.20397E-11 | 2.57463E-21 | 4.54472E-14 |
| **Phenyl ethanol** | 3.20778E-16 | 6.12805E-21 | 1.86376E-19 |
| **Styrene** | 1.30511E-15 | 8.61611E-21 | 7.84042E-16 |
| **Nonyl acetate** | 7.66464E-15 | 1.02628E-20 | 7.78033E-19 |
| **Butanoic acid** | 9.11509E-16 | 2.68329E-20 | 9.44188E-17 |
| **1-Heptanol** | 1.32354E-24 | 7.20754E-20 | 4.85246E-21 |
| **Octanoic acid** | 3.72728E-18 | 1.02791E-19 | 5.54223E-18 |
| **1-Propanol** | 2.44563E-20 | 2.51465E-19 | 1.6293E-21 |
| **Hexyl acetate** | 2.32887E-13 | 3.02165E-19 | 2.26572E-20 |
| **Ethyl acetate** | 2.28162E-12 | 5.19429E-19 | 1.11605E-19 |
| **2-Methyl-1-propanol** | 2.83673E-15 | 5.79771E-19 | 3.26686E-20 |
| **Heptanoic acid** | 1.5779E-14 | 9.353E-19 | 7.80402E-20 |
| **Ethyl 2-methylpropanoate** | 8.75989E-14 | 4.52388E-18 | 7.21527E-15 |
| **Pentyl acetate** | 4.84896E-11 | 1.68031E-17 | 1.56413E-18 |
| **1-Nonanol** | 7.3287E-17 | 1.77986E-17 | 5.22497E-16 |
| **1-Decanol** | 1.5631E-19 | 2.02826E-17 | 4.94009E-18 |
| **2-Methyl-2,3-pentanediol** | 2.05751E-18 | 9.31283E-17 | 3.35937E-18 |
| **(*Z*)-2-Pentenyl acetate** | 3.62277E-12 | 9.41489E-17 | 1.19475E-16 |
| **Ethyl 3-methylbutanoate** | 1.00484E-10 | 3.74199E-16 | 1.1266E-11 |
| **2-Methylbutyl acetate + 3-methylbytyl acetate** | 6.06872E-08 | 1.81113E-15 | 6.31398E-13 |
| **2-Hydroxy-3-pentanone** | 9.36231E-16 | 3.78008E-15 | 1.64627E-16 |
| **Octane** | 5.81433E-13 | 4.40872E-15 | 1.69403E-08 |
| **(*E*,*E*)-2,4-Hexadienal** | 8.31398E-06 | 6.29808E-15 | 0.51512448 |
| **Ethyl nonanoate** | 1.20573E-13 | 8.52192E-15 | 2.05218E-14 |
| **Ethyl octanoate** | 8.81802E-15 | 1.09819E-14 | 2.09877E-16 |
| **2,2-Dimethyl-1-propanol** | 7.41256E-17 | 3.13559E-14 | 4.89792E-13 |

| | | | |
|---|---|---|---|
| **(*Z*)-3-Hexenyl acetate** | 1.67812E-08 | 3.6027E-14 | 1.64593E-15 |
| **Limonene** | 0.047314201 | 8.70377E-14 | 0.005347179 |
| **Ethyl decanoate** | 3.76224E-13 | 8.99621E-14 | 1.09778E-15 |
| **Benzyl Alcohol** | 1.69957E-10 | 9.61069E-14 | 3.42946E-13 |
| **1-Hexanol** | 3.07861E-12 | 1.12244E-13 | 7.45523E-11 |
| **Methyl propanoate** | 2.94579E-10 | 1.64078E-13 | 4.01576E-10 |
| **1-Butanol** | 3.11612E-08 | 1.81544E-13 | 5.55057E-10 |
| **2,2-Dimethyl propanoic acid** | 3.71133E-10 | 2.4585E-13 | 6.49333E-14 |
| **3-Hydroxy-2-butanone (acetoin)** | 2.15772E-13 | 7.49771E-13 | 8.6821E-16 |
| **Heptyl acetate** | 4.97871E-06 | 8.75673E-13 | 3.0088E-08 |
| **Methyl octanoate** | 1.80574E-17 | 1.11211E-12 | 5.74551E-15 |
| **(*Z*)-3-hexenal** | 0.000160964 | 3.2284E-12 | *0.652685924* |
| **Ethyl butanoate** | 1.02561E-08 | 5.86089E-12 | 7.89313E-13 |
| **(*E*)-2 Hexenal** | 1.36725E-06 | 6.48132E-12 | 0.27562446 |
| **2-Octanone** | 8.39845E-07 | 7.8548E-12 | 7.98519E-05 |
| **Ethyl 3-methyl-2-butenoate** | 1.52636E-05 | 1.14437E-11 | *0.251118742* |
| **Isobutylacetate** | 1.65955E-06 | 1.229E-11 | 1.51702E-11 |
| **Ethyl propanoate** | 1.12307E-07 | 1.27068E-11 | 3.09163E-12 |
| **1-Penten-3-one** | 0.031401343 | 2.68036E-11 | *0.710576889* |
| **1-Pentanol** | 5.82448E-15 | 3.38804E-11 | 3.49085E-12 |
| **Ethyl heptanoate** | 7.42789E-08 | 3.80106E-11 | 3.71183E-10 |
| **Ethanol** | 3.44778E-11 | 4.50196E-11 | 2.45636E-12 |
| **1-Hydroxy-2-propanone** | 3.55261E-09 | 8.21599E-10 | 2.12795E-12 |
| **(*E*)-2-Pentenal** | 1.31277E-05 | 2.25531E-09 | *0.251458378* |
| **2,2-Dimethyl-1-propyl acetate** | 1.33887E-09 | 2.43726E-09 | 1.20159E-11 |
| **Methyl decanoate** | 4.6237E-12 | 3.43057E-09 | 5.05552E-11 |
| **(*E*)-2-Hexen-1-ol** | 2.57136E-12 | 3.98599E-09 | 4.32823E-11 |
| **(*E*)-2-Penten-1-ol** | 1.17579E-08 | 6.03044E-09 | 8.91969E-05 |
| **1-Octanol** | 5.66564E-12 | 7.76138E-09 | 7.1712E-10 |
| **Methyl heptanoate** | 0.000532332 | 1.11892E-08 | 6.97416E-06 |
| **(*E*)-3-Hexen-1-ol** | 7.88218E-17 | 2.08154E-08 | 4.00032E-10 |
| **2-Pentanol** | *0.33304922* | 3.5473E-08 | 0.000926408 |
| **4-Ethyl-phenol** | 1.8675E-07 | 3.66565E-08 | 2.77354E-10 |
| **2,3-Butanedione** | 8.17689E-06 | 4.0649E-08 | 0.000337648 |
| **Nonanoic acid** | 1.99196E-08 | 1.9425E-07 | 1.85567E-09 |
| **Ethyl pentanoate** | 0.000783374 | 6.01108E-07 | 1.04444E-08 |
| **(*Z*)-2-Hexen-1-ol** | 2.62659E-15 | 6.40125E-07 | 5.98001E-08 |
| **(*Z*)-3-Hexen-1-ol** | 4.0564E-08 | 2.41197E-06 | 4.41281E-09 |
| **(*Z*)-2-Penten-1-ol** | 8.3516E-07 | 4.15549E-06 | 0.022741744 |
| **2-Heptanol** | 0.017573029 | 6.51461E-06 | 0.002214252 |
| **Hexanal** | 0.004939952 | 2.67279E-05 | *0.104184313* |
| **2-Heptanone** | *0.840768764* | 0.000124289 | *0.085356588* |
| **Octanal** | 0.001382303 | 0.000175684 | *0.213637054* |
| **3-Methylbutanal** | 0.002716883 | 0.000194814 | 0.010794553 |
| **Heptanal** | 0.004086507 | 0.000195405 | 0.037380242 |
| **(*E*)-2-Heptenal** | 0.000107487 | 0.000203516 | *0.087413602* |
| **(*E*)-2-Octenal** | 0.00078261 | 0.000711534 | *0.141736992* |
| **(*E*,*E*)-2,4-Nonadienal** | 0.000930442 | 0.001208263 | 0.032599937 |
| **2-Methylbutanal** | 0.002970931 | 0.001446163 | 0.023243709 |
| **2-Methylpropanal** | 0.013816763 | 0.001957445 | *0.080941771* |
| **Methyl isobutyl ketone** | 0.001025987 | 0.002037944 | 0.000178994 |
| **Pentanal** | *0.128395638* | 0.002474495 | 0.007157624 |
| **1-Penten-3-ol** | 5.12522E-05 | 0.002780428 | *0.420032735* |
| **(*E*,*E*)-2,4-Heptadienal** | 0.000254386 | 0.003066809 | *0.142757234* |

| | | | |
|---|---|---|---|
| **(*E*)-2-Decenal** | 0.010327312 | 0.003249809 | *0.073592893* |
| **Methanol** | 9.30286E-09 | 0.00674298 | 0.025769557 |
| **4-Hexen-2-one** | 2.64845E-08 | 0.014508132 | 0.007102205 |
| **3-Pentanone** | 0.00460309 | 0.019540282 | 4.3788E-05 |
| **Methyl nonanoate** | 4.01902E-05 | 0.022199507 | 0.008174644 |
| **Acetaldehyde** | 0.006019301 | 0.022964923 | 2.57121E-08 |
| **(*E*,*E*)-2,4-Decadienal** | 0.003967724 | 0.037448943 | *0.566879943* |
| **Nonanal** | 0.046950542 | *0.052879679* | *0.362236777* |
| **6-Methyl-5-hepten-2-one** | *0.06526592* | *0.074896564* | *0.656242764* |
| **Benzaldehyde** | 9.60959E-08 | *0.079269703* | 9.05797E-08 |
| **Heptane** | *0.129495071* | *0.20436331* | *0.679727785* |
| **Butanone** | 0.003522836 | *0.255692685* | 0.006072708 |
| **Toluene** | *0.241279217* | *0.290491842* | *0.535406712* |