SUPPLEMENTARY MATERIAL

Comparison Of Essential Oils From Cistus Species Growing In Sardinia

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Abstract

Cistus genus is present in Sardinia with large populations of C. monspeliensis, C. salvifolius, C. creticus subsp. eriocephalus and few stations of C. albidus, C. creticus subsp. creticus and C. creticus subsp. corsicus. No chemical studies are currently being carried on Cistus species of Sardinia. The essential oils have shown six different profiles. C. creticus subsp. eriocephalus showed a high amount of manoyl oxide and its isomer (70%). C. salvifolius has pointed out the group of labdans, (20%); another consistent percentage is made of perfumed molecules as ionone and its derivate. Several linear hydrocarbons were produced by C. monspeliensis, and the heneicosane was the most represented element. In C. albidus no labdane-type diterpenes were identified. Analysis of C. creticus subsp creticus revealed several oxygenated sesquiterpenes and labdane-type diterpenes, especially manoyl oxide. C. creticus subsp. corsicus was qualitatively very similar to C. creticus subsp. creticus, notably concerning the labdane-type compounds.

Keywords: Cistus, essential oil, labdane, manoyl oxide
| RI   | Components                        | C. albidus | C. creticus  | C. creticus  | C. creticus  | C. monspeliensis | C. salvifolius | IDa | References |
|------|-----------------------------------|------------|--------------|--------------|--------------|-----------------|----------------|-----|------------|
|      |                                   |            | subsp. corsicus | subsp. creticus | subsp. eriocephalus |                  |                |     |            |
| 2021 | 3-methyl eicosane                 |            |              |              |              |                 |                |     |            |
| 2100 | heneicosane                       |            |              |              |              |                 |                |     | RI, MS     |
| 2400 | tetracosane                       |            |              |              |              |                 |                |     | Std        |
| 2700 | heptacosane                       |            |              |              |              |                 |                |     | Std        |
|      |                                   |            |              |              | te            |                 |                |     |            |
|      |                                   |            |              |              |              |                 |                |     |            |
|      |                                   |            |              |              |              |                 |                |     |            |
| 1101 | nonanal                           |            |              | 0.12         |              |                 |                |     | Std        |
| 1320 | 5,9-dimethyl-5,8-decadien-2-one   |            |              |              |              |                 |                |     | RI, MS     |
| 1327 | undecanal                         |            |              | 0.35         |              |                 |                |     | Std        |
| 1333 | 2,6,6-trimethyl 1-cyclohexene-1-acetaldehyde | 0.24         |              |              |              |                 |                |     | RI, MS     |
| 1348 | 6-methyl-5-(1-methylethylidene)-6,8-nonadien-2-one | 1.41         |              |              |              |                 |                |     | RI, MS     |
| 1401 | 4-(4-methyl phenyl)-pentanal      |            |              |              |              |                 |                |     | RI, MS     |
| 1409 | dodecanal                         |            |              | 0.32         |              |                 |                |     | Std        |
| 1826 | hexahydrofarnesyl acetone [(+/-)-phytene] |            |              | 6.55         |              |                 |                |     | RI, MS     |
| Compound                                      | Retention Index (RI) | Similarity (MS) | Authors & Year |
|-----------------------------------------------|----------------------|-----------------|----------------|
| cis,cis,cis-7,10,13-hexadecatrienal           | 0.39                 |                 |                |
| 15-methyl-(Z)-11-hexadecenal                 | 0.51                 | 0.26            |                |
| **FATTY ACIDS**                               |                      |                 |                |
| lauric acid                                  | 0.81                 |                 |                |
| miristic acid                                | 1.09                 |                 |                |
| palmitic acid                                | 1.45                 |                 |                |
| **ALIPHATIC ESTERS**                         |                      |                 |                |
| methoxyacetic acid-2-ethylcyclohexyl ester   | 0.48                 |                 |                |
| **AROMATIC ESTERS**                          |                      |                 |                |
| (3Z)-2-hexenyl benzoate                      | 2.80                 | 0.45            | Hazzit, Baaliouamer, et al., 2006 |
| (2E)-2-hexenyl benzoate                      | 0.38                 |                 | Campeol, Flamini, et al., 2001 |
| benzyl benzoate                              | 0.95                 |                 | Su, Ho, et al., 2006 |
| benzyloleate                                 | 0.32                 | 0.27            |                |
| **MONOTERPENE HYDROCARBONS**                 |                      |                 |                |
| α-pinene                                     | 0.36                 |                 |                |
| camphene                                     | 0.16                 |                 |                |
| β-pinene                                     | 0.21                 |                 |                |
| limonene                                     | 0.12                 |                 |                |
| **OXIGENATED MONOTERPENES**                  |                      |                 |                |
| borneol                                      | 0.49                 |                 |                |
| terpinen-4-ol                                | 0.26                 |                 |                |
| Compound                              | RI  | MS  | Std  |
|--------------------------------------|-----|-----|------|
| α-terpineol                          | 0.42| 0.40|      |
| β-caryophyllene                      |     |     |      |
| ascaridole                           | 0.29| RI, MS | Lucero, Estell, et al., 2003 |
| 10-(acetyl methyl)-3-carene          | 0.79| RI, MS | Al-Qudah, 2013 |

**SESQUITERPENE HYDROCARBONS**

| Compound                              | RI  | MS  | Std  |
|--------------------------------------|-----|-----|------|
| α-cubebene                           | 0.1 | 0.49| 0.17 |
| α-copaene                            |     |     | 0.45 |
| (-)-β-bourbonene                     | 4.88| 0.93| 1.38 |
| cis-α-bergamotene                    | 0.61| 0.33|      |
| E-α-ionene                           |     |     | 0.73 |
| E-β-caryophyllene                    | 4.54| 0.92| 1.18 |
| β-copaene                            | 0.77| 0.32|      |
| α-guaiene                            |     | 0.27| 0.47 |
| aromadendrene                        | 0.98|     | 0.09 |
| β-Z-farnesene                        | 1.79|     | 0.46 |
| α-humulene                           | 1.04|     |      |
| β-E-farnesene                        |     | 0.43|      |
| muurola-4,11-diene                   | 2.54|     |      |
| cis-muurola-4(14)5-diene             |     |     | 0.17 |
| alloaromadendrene                    | 5.32|     | 1.97 |
| α-curcumene (= ar curcumene)         | 16.01|     | 0.72 |
| D-germacrene                         | 3.57| 0.64| 0.27 |
| α-zingiberene                        | 3.53|     | 2.33 |

Weyerstahl, Marschall, et al., 1999
| Ret. | Compound                        | RI  | Std  | MS   | Ref                                           |
|------|---------------------------------|-----|------|------|-----------------------------------------------|
| 1498 | α-selinene                      | 2.09| 0.50 |      |                                               |
| 1498 | viridiflorene                   | 0.90|      |      |                                               |
| 1480 | γ–muurolene                     | 0.97| 0.96 | 0.46 |                                               |
| 1500 | α-muurolene                     | 2.04| 1.39 | 1.80 | 1.15  | 1.92  | 0.38 | RI, MS                                      |
| 1502 | γ-patchoulene                    | 0.77|      |      |                                               |
| 1505 | β-himachalene                   | 0.66|      |      |                                               |
| 1514 | γ–cadinene                      | 2.45| 1.98 | 1.17 | 0.71  |                                               |
| 1515 | γ-bisabolene                    | 1.25|      |      |                                               |
| 1523 | δ-cadinene                      | 6.70| 7.67 | 2.18 | 2.51  | 0.12  | RI, MS                                      |
| 1528 | cada-1,4-diene                   | 1.02|      | 0.85 |                                               |
| 1539 | α-cadinene                      | 1.67|      |      |                                               |
| 1566 | β-calacorene                    | 0.71| 0.47 | 0.26 | 0.50  | RI, MS                                      |
| 1677 | cadalene                        | 0.33|      | 0.28 | 1.07  | RI, MS                                      |

**OXYGENATED SESQUITERPENES**

| Ret. | Compound                        | RI  | Std  | MS   | Ref                                           |
|------|---------------------------------|-----|------|------|-----------------------------------------------|
| 1177 | terpinen 4-ol                   | 0.26|      |      |                                               |
| 1189 | α-terpineol                     | 0.42| 0.40 |      |                                               |
| 1498 | 6-epi-shyobunone                | 1.13|      |      |                                               |
| 1510 | shyobunone                      | 1.43|      |      |                                               |
| 1566 | cis-(Z)-α-bisabolene epoxide    | 0.80|      |      |                                               |
| 1567 | isoaromadendrene epoxide        | 4.86|      |      |                                               |
| 1578 | spathulenol                     | 0.65| 0.31 | 0.36 | 0.42  | 0.18  | RI, MS                                      |
| 1580 | trans-(Z)-α-bisabolene epoxide  |      |      |      |                                               |
| 1583 | caryophyllene oxide             | 0.80| 0.40 | 0.24 | 0.53  | 0.21  | Std                                          | Hamm, Bleton, et al., 2005 |
| Compound                        | RI 1 | RI 2 | RI 3 | RI 4 | Std |
|--------------------------------|------|------|------|------|-----|
| globulol                       | 2.22 | 0.86 | 0.95 | 3.80 | 0.13 |
| viridiflorol                   | 2.51 | 0.43 | 1.56 | 0.74 | Std |
| aromadendrene oxide-(2)       | 0.58 |      |      |      | Std |
| cubedol                        | 0.30 | 0.28 | 0.88 |      | RI, MS |
| guaiol                         | 1.26 | 2.49 | 8.80 | 0.36 | Std |
| δ-cadinol                      | 3.02 | 6.47 | 4.86 | 2.82 | 2.23 | 0.64 | RI, MS |
| τ-murolol                      | 1.81 | 0.93 | 0.92 | 0.68 |      | RI, MS |
| *cis*-cadin-4-en-7-ol          | 7.43 |      |      | 5.03 |      | RI, MS | Su, Ho, et al., 2006 |
| τ-cadinol                      | 6.22 | 13.63| 3.47 | 3.37 |      | RI, MS |
| selina-3,11-dien-6-α-ol        | 4.23 | 18.04|      |      |      | RI, MS |
| selin-11-en-4-α-ol             | 15.55| 0.69 | 1.55 |      |      | RI, MS |
| *7*-epi-α-eudesmol             | 2.73 |      |      |      |      | RI, MS |
| α-bisabolol                    | 3.59 |      | 1.07 |      |      | Std |
| ambroxide                      |      | 0.23 |      | 0.75 |      | Std |
| alloaromadendrolβ              |      |      |      | 0.57 |      | RI, MS |

**NORISOPRENOIDS**

| Compound                        | RI 1 | RI 2 | RI 3 | Std |
|--------------------------------|------|------|------|-----|
| β-cyclocitral                  |      |      | 0.31 | Std |
| dehydro-ar-ionene              |      |      | 0.50 | RI, MS |
| (E)-β-damascenone              |      |      | 0.13 | Std |
| dihydro-α-ionone               |      |      | 0.75 | RI, MS |
| β-iso-ionone                   |      |      | 2.47 | RI, MS |
| α-ionene                       |      |      | 0.73 | RI, MS |
| α-ionone                       |      |      | 1.32 | Std |
| 7,8-dihydro-β-ionone           |      |      | 3.89 | RI, MS |
| Year | Compound Description | RI | MS | Std |
|------|----------------------|----|----|-----|
| 1962 | geranyl-α-terpinene   | 2.13 | RI, MS | Paolini et al., 2008 |
| 1965 | geranyl-p-cymene      | 9.61 | RI, MS | Paolini et al., 2008 |
| 1969 | cembrene A (3Z)       | 1.42 | RI, MS | Rahimi-Nasrabadi, Gholivand, et al., 2009 |
|      |                      |     |     |     |
| 1972 | cembrene A (3E)       | 8.55 | RI, MS | Rahimi-Nasrabadi, Gholivand, et al., 2009 |
| 2017 | kaur-16-ene           | 1.30 | RI, MS | Demetzos et al., 2002 |
| 2049 | phytol               | 4.01 | Std |     |
| 1998 | manoyl oxide          | 0.18 | 2.47 | 8.17 | 64.00 | 11.98 | RI, MS | Demetzos et al., 2002 |
| 1985 | manoyl oxide isomer   |     | 4.40 |     |     | 2.10 | RI, MS | Demetzos et al., 2002 |
| 2017 | 13-epi-manoyl oxide   | 2.46 | RI, MS | Demetzos et al., 2002 |
| 2097 | dihydromanoyl oxide   |     | 0.77 |     |     |     | RI, MS |     |
| 1825 | sclareol oxide (trans-A/B) | 1.06 | RI, MS | Wulfson et al., 1966 |
| 1846 | sclareol oxide (cis-A/B) | 0.40 | 2.07 | 1.10 | 6.07 | RI, MS | Wulfson et al., 1966 |
|      |                      |     |     |     |     |     |     | Hutschenreuther et |
| Compounds | RI     | MS     | Compounds | RI     | MS     |
|-----------|--------|--------|-----------|--------|--------|
| Labdane unidentified (MW 281) | 1.24   |        | Labdane unidentified (MW 281) | 1.21   | 1.24   | 1.50 |
| Labdane unidentified (MW 281) | 1.77   | RI, MS | Hutschenreuther et al., 2010 |
| Sclareol oxide (cis B/C) | 1.47   | RI, MS |
| 1967      |        |        | 1983      | 11.66  | 1.46   | 0.36 |
| 1983      |        |        | 1996      | 1.78   | 5.95   |      |
| 2057      |        |        | 2022      | 21.07  | 20.26  | 2.82 |
| 2223      |        |        | Others    | 3.70   | 0.78   |      |
| 1381      |        |        | 1,1-dimethyl-2-(2-methyl-1-propenyl)-cyclopropane | 0.49   |        |
| 1702      | hexadecanol | 1.56   | Std       |
|           | cistodiol |        | Std       |
|           |         |        |           |
|           | 99.43   | 97.6   | 99.26     | 94.15  | 92.15  | 81.27 |

Table S1. Chemical composition of the essential oils of *Cistus* species growing wild in Sardinia

*Identification methods: MS by comparison of the Mass spectrum with those of the computer mass libraries Adams, Nist 11 and by interpretation of the mass spectra fragmentations. RI by comparison of retention index with those reported in literature. Std by comparison of the retention time and mass spectrum of available authentic standards.*
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