**Theoretical modeling and experimental studies of Terebinthextracts as green corrosion inhibitors for iron in 3% NaCl medium**

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**S1: Gas chromatographic-Mass spectral analysis**

 The analyzes process of the Terebinth EOs was carried out using Perkin Elmer Clarus SQ 8C Gas chromatograph coupled with a mass spectrometer (GC/MS), equipped with a Rxi-5MS capillary column (30 m x 0.25 mm, film thickness 0.25 µm). The carrier gas was helium (He: 1 mL/min. Temperature program: For the first 2 min the oven temperature was kept at 40°C and then increased at a rate of 4°C/min until reached a temperature of 180°C and from 180 to 300 at a rate of 20°C/min and then held isothermally at 300°C for 2 min. As regards the split injection was conducted with a ratio split of 1/20, the injected volume: 1 µL. Injector and detector temperature were held at 220°C. Ion source temperature: 200°C; energy ionization: 70eV; electron ionization mass spectra were acquired oven the mass range 40-450 Da. The chemical components of Terebinth EOs were identified by their retention indices, as well as the mass spectra with those on the stored in NIST library-version 2014. For the Kovats index were estimated using to the retention time of series of n-alkanes (C8-C20).

**S2: Table** Composition of Terebinthessential oils

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Peak | Compounds | Chemical Formula | Kovats indice | Terebinth |
| Twigs | Leaves | Fruits |
| 12 | α-Pinene | C10H16 | 936 | **36.81** | **50.58** | **32.65** |
| Camphene | C10H16 | 949 | 0.98 | 0.88 | 1.03 |
| 3 | β-Pinene | C10H16 | 978 | 4.64 | 2.41 | 2.98 |
| 4 | β-Myrcene | C10H16 | 993 | 3.50 | 1.72 | 1.16 |
| 5 | δ-3-Carene | C10H16 | 1011 | - | 1.12 | 1.09 |
| 6 | p-Cymene | C10H16 | 1026 | 1.70 | 1.24 | 1.70 |
| 7 | Limonene | C10H16 | 1030 | **6.88** | **13.96** | **15.07** |
| 8 | trans-β-Ocimene | C10H16 | 1050 | - | 1.03 | tr |
| 9 | Terpinolene | C10H16 | 1089 | 1.22 | 5.44 | 4.85 |
| 10 | Linalool | C10H18O | 1100 | tr | - | 1.03 |
| 11 | trans-Pinocarveol | C10H16O | 1139 | 0.79 | - | 1.31 |
| 12 | trans-Verbenol | C10H16O | 1147 | 1.72 | tr | 1.11 |
| 13 | Pinocarvone | C10H14O | 1162 | 1.16 | - | tr |
| 14 | Borneol | C10H18O | 1166 | 0.97 | tr | 0.86 |
| 15 | Terpinen-4-ol | C10H18O | 1176 | 1.58 | 0.85 | 0.91 |
| 16 | p-Cymen-8-ol | C10H14O | 1182 | 1.85 | 1.76 | 1.65 |
| 17 | α-Terpineol | C10H18O | 1184 | **3.97** | **2.50** | **5.15** |
| 18 | Myrtenol | C10H16O | 1195 | 1.52 | - | 0.77 |
| 19 | Verbinone | C10H14O | 1207 | 1.21 | - | tr |
| 20 | cis-Carveol | C10H16O | 1222 | 0.53 | - | tr |
| 21 | Piperitone | C10H18O | 1252 | - | tr | 0.77 |
| 22 | Bornyl acetate | C12H20O2 | 1284 | - | 0.48 | - |
| 23 | Undecan-2-one | C11H22O | 1290 | 3.70 | 0.88 | 1.27 |
| 24 | Myrtenyl acetate | C12H18O2 | 1323 | 0.51 | tr | 0.72 |
| 25 | α-Ylangene | C15H24 | 1370 | tr | - | 0.91 |
| 26 | α-Copaene | C15H24 | 1374 | 2.18 | tr | 0.71 |
| 27 | β-Bourbonene | C15H24 | 1384 | - | tr | 0.83 |
| 28 | β-Elemene | C15H24 | 1389 | tr | tr | 0.56 |
| 29 | α-Gurjunene | C15H24 | 1396 | 2.75 | - | - |
| 30 | β-Caryophyllene | C15H24 | 1417 | tr | 2.19 | 1.03 |
| 31 | α-Humulene | C15H24 | 1451 | 1.16 | 1.84 | 1.03 |
| 32 | γ-Muurolene | C15H24 | 1473 | 1.97 | 1.32 | 2.43 |
| 33 | Germacrene D | C15H24 | 1477 | - | 1.89 | 1.37 |
| 34 | Epicubebol | C15H24 | 1491 | tr | 0.47 | 0.92 |
| 35 | α-Muurolene | C15H24 | 1497 | 0.61 | 0.61 | 1.02 |
| 36 | γ-Cadinene | C15H24 | 1510 | 1.39 | 1.06 | 1.47 |
| 37 | δ-Cadinene | C15H24 | 1531 | 0.56 | 1.85 | 3.01 |
| 38 | α-Cadinene | C15H24 | 1550 | 0.61 | tr | 0.53 |
| 39 | Selina-3,7(11)-diene | C15H24 | 1557 | tr | - | 1.61 |
| 40 | Spathulenol | C15H24O | 1574 | 0.73 | - | - |
| 41 | Caryophyllene oxide | C15H24O | 1580 | 1.92 | 0.79 | 0.58 |
| 42 | Humulene epoxide II | C15H24O | 1606 | 1.81 | tr | 1.18 |
| 43 | τ-Muurolol | C15H26O | 1637 | 0.67 | tr | 0.48 |
| 44 | β-Eudesmol | C15H26O | 1646 | 0.65 | tr | 0.50 |
| 45 | α-Cadinol | C15H26O | 1649 | 1.51 | 1.14 | 0.95 |
| 46 | Platambin | C15H26O2 | 1839 | 0.90 | - | 0.52 |
| 47 | m-Camphorene | C20H32 | 1902 | 0.82 | - | 1.27 |
| 48 | (E,E)-Geranyllinalool | C20H34O | 2025 | 3.26 | 0.45 | 0.54 |
|  | Total (%) |  |  | 98,74 | 98,48 | 99,53 |

tr:trace (<0.2); –: Not detected

**S3:**



**Fig.** Variation of the open-circuit potential for iron in 3% NaCl without and with 3000 ppm of Terebinth essential oils.

**S4:**



**Fig.** FTIR Spectrum (a) of Terebinth fruit essential oil and (b) thin film formed on the iron surface immersed in 3% NaCl containing 3000 ppm of Terebinth fruit essential oil.

**S5: Table** Calculated Fukui functions for the compounds inhibitors.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| α-Pinene | Limonene | α-Terpineol | p-Cymene  | p-Cymene-8-ol |
|  | f- | f+ |  | f- | f+ |  | f- | f+ |  | f- | f+ |  | f- | f+ |
| C(1) | -0.020 | -0.024 | C(1) | -0.028 | -0.026 | C(1) | -0.034 | -0.042 | C(1) | 0.070 | 0.006 | C(1) | 0.066 | 0.038 |
| C(2) | -0.012 | -0.009 | C(2) | -0.032 | -0.033 | C(2) | -0.025 | -0.025 | C(2) | 0.040 | 0.052 | C(2) | 0.035 | 0.016 |
| C(3) | -0.039 | -0.046 | C(3) | -0.017 | -0.023 | C(3) | -0.021 | -0.022 | C(3) | 0.047 | 0.127 | C(3) | 0.039 | 0.124 |
| C(4) | 0.146 | 0.167 | C(4) | -0.042 | -0.029 | C(4) | -0.034 | -0.040 | C(4) | 0.075 | 0.010 | C(4) | 0.073 | 0.055 |
| C(5) | 0.099 | 0.141 | C(5) | 0.132 | 0.054 | C (5) | 0.154 | 0.164 | C(5) | 0.043 | 0.052 | C(5) | 0.036 | 0.014 |
| C(6) | -0.005 | -0.013 | C(6) | 0.104 | 0.058 | C(6) | 0.110 | 0.111 | C(6) | 0.046 | 0.125 | C(6) | 0.043 | 0.122 |
| C(7) | -0.037 | -0.042 | C(7) | -0.026 | -0.020 | C(7) | -0.031 | -0.036 | C(7) | -0.027 | -0.028 | C(7) | -0.023 | -0.029 |
| C(8) | -0.021 | -0.018 | H(8) | 0.071 | 0.056 | C(8) | -0.014 | -0.015 | C(8) | -0.030 | -0.027 | C(8) | -0.028 | -0.017 |
| C(9) | -0.027 | -0.028 | H(9) | 0.067 | 0.061 | C(9) | -0.016 | -0.017 | C(9) | -0.024 | -0.021 | C(9) | -0.020 | -0.021 |
| C(10) | -0.020 | -0.019 | H(10) | 0.057 | 0.043 | C(10) | -0.017 | -0.019 | C(10) | -0.024 | -0.021 | C(10) | -0.020 | -0.021 |
| H(11) | 0.059 | 0.058 | H(11) | 0.027 | 0.024 | O(11) | 0.017 | 0.016 | H(11) | 0.081 | 0.087 | O(11) | 0.051 | 0.009 |
| H(12) | 0.087 | 0.080 | H(12) | 0.062 | 0.038 | H(12) | 0.079 | 0.080 | H(12) | 0.077 | 0.090 | H(12) | 0.032 | 0.027 |
| H(13) | 0.085 | 0.078 | H(13) | 0.075 | 0.051 | H(13) | 0.084 | 0.095 | H(13) | 0.080 | 0.085 | H(13) | 0.077 | 0.083 |
| H(14) | 0.110 | 0.107 | H(14) | 0.099 | 0.070 | H(14) | 0.031 | 0.033 | H(14) | 0.083 | 0.096 | H(14) | 0.072 | 0.087 |
| H(15) | 0.066 | 0.064 | H(15) | 0.075 | 0.051 | H(15) | 0.055 | 0.053 | H(15) | 0.074 | 0.053 | H(15) | 0.069 | 0.077 |
| H(16) | 0.085 | 0.085 | H(16) | 0.066 | 0.044 | H(16) | 0.027 | 0.031 | H(16) | 0.059 | 0.050 | H(16) | 0.079 | 0.092 |
| H(17) | 0.057 | 0.059 | H(17) | 0.050 | 0.040 | H(17) | 0.078 | 0.071 | H(17) | 0.059 | 0.047 | H(17) | 0.055 | 0.049 |
| H(18) | 0.081 | 0.078 | C(18) | 0.006 | 0.079 | H(18) | 0.081 | 0.079 | H(18) | 0.048 | 0.040 | H(18) | 0.054 | 0.054 |
| H(19) | 0.043 | 0.039 | C(19) | 0.046 | 0.121 | H(19) | 0.111 | 0.107 | H(19) | 0.058 | 0.051 | H(19) | 0.067 | 0.060 |
| H(20) | 0.030 | 0.028 | C(20) | -0.012 | -0.025 | H(20) | 0.085 | 0.084 | H(20) | 0.026 | 0.017 | H(20) | 0.032 | 0.022 |
| H(21) | 0.037 | 0.034 | H(21) | 0.034 | 0.048 | H(21) | 0.084 | 0.087 | H(21) | 0.028 | 0.021 | H(21) | 0.059 | 0.053 |
| H(22) | 0.049 | 0.048 | H(22) | 0.060 | 0.084 | H(22) | 0.058 | 0.058 | H(22) | 0.028 | 0.021 | H(22) | 0.031 | 0.016 |
| H(23) | 0.043 | 0.039 | H(23) | 0.029 | 0.066 | H(23) | 0.037 | 0.038 | H(23) | 0.026 | 0.017 | H(23) | 0.032 | 0.022 |
| H(24) | 0.001 | -0.003 | H(24) | 0.034 | 0.062 | H(24) | 0.016 | 0.016 | H(24) | 0.058 | 0.051 | H(24) | 0.031 | 0.016 |
| H(25) | 0.068 | 0.063 | H(25) | 0.036 | 0.053 | H(25) | 0.014 | 0.014 |  |  |  | H(25) | 0.059 | 0.053 |
| H(26) | 0.038 | 0.034 | H(26) | 0.027 | 0.051 | H(26) | 0.040 | 0.042 |  |  |  |  |  |  |
|  |  |  |  |  |  | H(27) | 0.016 | 0.016 |  |  |  |  |  |  |
|  |  |  |  |  |  | H(28) | 0.005 | 0.009 |  |  |  |  |  |  |
|  |  |  |  |  |  | H(29) | 0.012 | 0.011 |  |  |  |  |  |  |

The Fukui functions or nucleophilic and electrophilic attacks are obtained from the following approximations (Geerlings et al., 2003):

$f\_{K}^{+}\left(r\right)=ρ\_{k}\left(N+1\right)-ρ\_{k}\left(N\right) Nucleophilic attack$ (1)

$f\_{K}^{-}\left(r\right)=ρ\_{k}\left(N\right)-ρ\_{k}\left(N-1\right) Electrophilic attack $ (2)

ρk(N), ρk(N-1) and ρk(N+1) are the gross electronic populations of the site k in neutral, cation and anion, respectively.

**Reference**

Geerlings, P., De Proft, F., Langenaeker, W., 2003. Conceptual density functional theory. Chem. Rev. 103, 1793-1873. https://doi.org/10.1021/cr990029p