

Linalool Oxidation Reaction with Air under Ultrasound and Microwave Irradiations

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ABSTRACT. The ultrasound and microwave assisted air-oxidation of tertiary terpene alcohol – racemic linalool was investigated at 40-80°C. The experiments were carried out in the solvent-free conditions by microwave and ultrasound irradiations (150-650 W) at frequencies of 2450 MHz and 25 kHz, respectively. The analyses of the oxidation reaction products were performed with GC/MS method (Agilent Technologies GC/MS, 7890B/5977A, USA). By air-oxidation of linalool under microwave and ultrasound irradiations the following monoterpene diols (C₁₀H₁₈O₂) are mainly formed: (3E)-2,6-dimethylocta-3,7-diene-2,6-diol; (2Z)-2,6-dimethylocta-2,7-diene-1,6-diol; (2E)-2,6-dimethylocta-2,7-diene-1,6-diol; 2,6-dimethylocta-1,7-diene-3,6-diol; 1-methyl-4-prop-1-en-2-ylcyclohexane-1,2-diol; in oxidation products are also (3S,5E)-3,7-dimethylocta-1,5,7-trien-3-ol, C₁₀H₁₆O and very insignificant quantities of cis- and trans-linalool oxides (furanoids, C₁₀H₁₈O₂) and 2-(5-ethenyl-5-methyloxolan-2-yl)propan-2-yl ethyl carbonate, C₁₃H₂₂O₄. With growth of power and time of ultrasonic and microwave irradiations the conversion of linalool reaches 65.6 and 52.4%, respectively; qualitatively the composition of products in both cases is identical. © 2019 Bull. Georg. Natl. Acad. Sci.

Key words: linalool, oxidation, monoterpene diols, microwave assisted reaction, ultrasound-promoted reaction

The effect of microwave (MW) and ultrasound (US) irradiations on conversion of terpene alcohols, was investigated in the oxidation reaction of linalool with pure air [1-3].

Studies on the oxidation of linalool in air are few. They are mainly devoted to the autoxidation of linalool at room temperature. It was shown that linalool oxidation on air exposure occurs slowly at

room temperature [4]. After 10 weeks of air exposure, about 20% of the linalool was converted. After about 30 weeks, 50% of the initial compound was consumed, and after 80 weeks only about 4% remained.

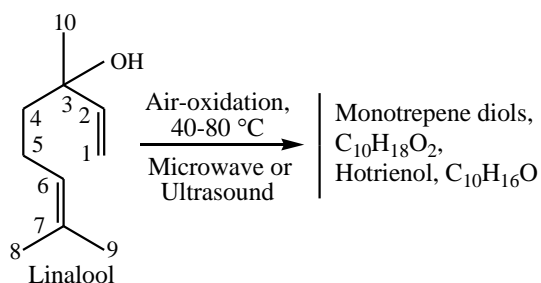
On air exposure oxidation reaction products of linalool at room temperature contain the following substances: allyl hydroperoxides (in the main 7-hydroperoxy-3,7-dimethylocta-1,5-diene-3-ol and an insignificant amount of 6-hydroperoxy-3,7-dimethylocta-1,7-diene-3-ol), the furan oxides and pyranoxides (2-(5-methyl-5-vinyltetrahydrofuran-2-yl)propan-2-ol; 2,2,6-trimethyl-6-vinyltetrahydro-2H-pyran-3-ol); also linalool alcohols (2,6-dimethylocta-3,7-diene-2,6-diol; 2,6-dimethylocta-1,7-diene-3,6-diol) and a little linalyl aldehyde (6-hydroxy-2,6-dimethylocta-2,7-dienal) were identified in the oxidation mixture [4-7].

Studies [5, 8] also showed that from the primary products of the autoxidation of allyl hydroperoxides, secondary oxidation products (alcohols, ketones, aldehydes, cis- and trans-linalool oxides of the furanoid and pyranoid forms) are subsequently formed. The observed linalool air-oxidation products spectrum was explained in terms of a direct reaction path, the ene-type mechanism, and the radical mechanism.

Linalool was heated in the presence of insufficient air at 40°C for 700 hours [9]. Among the 26 identified reaction products the most prominent were four isomeric linalool oxides identified as cis- and trans-linalool oxide (furanoid) and cis- and trans-linalool oxide (pyranoid) [9]. Also, in the reaction mixture, there are 2,6-dimethylocta-2,7-diene-1,6-diol (8-Hydroxylinalool) and 3,7-dimethylocta-1,5,7-trien-3-ol (Hotrienol).

In the present study, we report on the effect of microwave and ultrasonic irradiations on the oxidation of terpene alcohol-linalool in the flow of pure air at 40-80°C; the research was carried out in order to identify the possibilities of obtaining of citral from linalool by its isomerization into geraniol and subsequent oxidation of the latter. In

the present study it turned out that by air-oxidation of linalool under microwave and ultrasound irradiations dihydroxylated products of linalool were mainly formed (Scheme).



Scheme. Air-oxidation of linalool under microwave and ultrasound irradiations.

Materials and Methods

Chemicals. Linalool (97-98 %, racemic GC, (\pm)-3,7-Dimethylocta-1,6-dien-3-ol) and methanol (for HPLC, $\geq 99.9\%$) were purchased from "Sigma-Aldrich"(USA).

Linalool oxidation-irradiation reaction procedure.

The oxidation of linalool with a pure air was carried out under direct ultrasonic or microwave irradiations in Ultrasonic-Microwave (hybrid) Reactor UMR-300B (Shinka, Japan) by ultrasonic vibration probe of 18 mm diameter, US frequency 25 kHz and at ultrasound and microwave output 150-650 W; in some cases, during the air-oxidation of linalool the combined effect of US and MW was also studied. The oxidation-irradiation reaction of linalool was conducted in a liquid phase in a 50 ml three-necked round-bottomed glass flask ("Bomex") with a reflux condenser, under solvent free condition and ambient pressure and at temperatures in the range of 40-80°C. Duration of run was 1-5 h, the conversion of 4-8 ml of linalool was examined, air was taken in excess; the molar ratio of linalool to air was varied in the range from 1/3 to 1/17.

Analysis of the reaction products. The analyses of the reaction products in solvent – methanol was

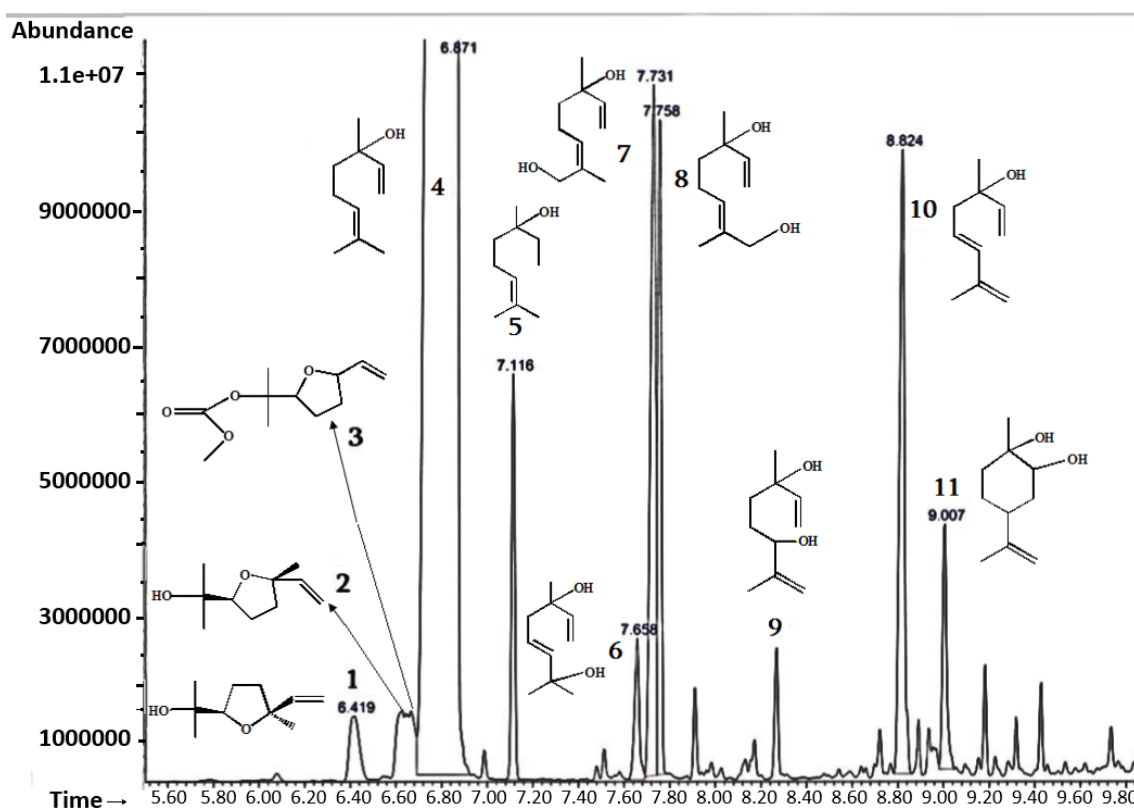


Fig.1. GC/MS Chromatogram and structures of the starting beta-linalool **4** and products (**1-3, 6-11**) of its ultrasound-assisted (450 W, 1 h) oxidation in a flow of pure air at 80°C. **1** – cis-Linalool oxide, furanoid C₁₀H₁₈O₂, **2** – trans-Linalool oxide, furanoid C₁₀H₁₈O₂, **3** – 2-(5-ethenyl-5-methyloxolan-2-yl)propan-2-yl ethyl carbonate C₁₃H₂₂O₄, **4** – 3,7-dimethylocta-1,6-diene-3-ol C₁₀H₁₈O, **5** – 1,2-Dihydrolinalool C₁₀H₂₀O, impurity substance of initial linalool, **6** – (3E)-2,6-dimethylocta-3,7-diene-2,6-diol C₁₀H₁₈O₂, **7** – (2Z)-2,6-dimethylocta-2,7-diene-1,6-diol C₁₀H₁₈O₂, **8** – (2E)-2,6-dimethylocta-2,7-diene-1,6-diol C₁₀H₁₈O₂, **9** – 2,6-dimethylocta-1,7-diene-3,6-diol C₁₀H₁₈O₂, **10** – (5E)-3,7-dimethylocta-1,5,7-trien-3-ol C₁₀H₁₆O, **11** – (1S,2R,4R)-1-methyl-4-prop-1-en-2-ylcyclohexane-1,2-diol C₁₀H₁₈O₂.

performed with GC/MS method (Agilent Technologies GC/MS, 7890B/5977A, USA) in the EI mode, 70 eV. There were used helium as a carrier gas and capillary column HP-5ms, Ultra Inert, 30 m x 0.32 mm x 0.25 μm. Analyses were carried out in program mode: hold at 80°C for 5 min, ramp to 210°C at 30°/min, hold at 210°C for 10 min. Helium was used as carrier gas at constant flow rate of 1.0 ml/min. The identification of the compounds was made by comparing the spectra with NIST 2014 library. The amount of linalool was determined from its calibration curve. Conversion of linalool was determined according to the formula: $C_{\text{Linalool, \%}} = \frac{(m_{\text{initial Linalool}} - m_{\text{Unconverted Linalool}}) \times 100}{m_{\text{initial Linalool}}}$, *m* is the mass of substance. The content of the reaction

products was compared in terms of GC-MS area%.

Results and Discussion

Linalool oxidation under irradiation of microwaves and ultrasounds. Under the influence of US and MW linalool **4** in the atmosphere of air at 40-80°C is oxidized to qualitatively same products (Fig. 1, Table); herewith the monoterpene diols (C₁₀H₁₈O₂) **6-9** and **11** were formed; in oxidation products were also (3S,5E)-3,7-dimethylocta-1,5,7-trien-3-ol **10**, C₁₀H₁₆O, very insignificant quantities of **1** cis- and **2** trans-linalool oxides (furanoid, C₁₀H₁₈O₂) and 2-(5-ethenyl-5-methyloxolan-2-yl)propan-2-yl ethyl carbonate **3**, C₁₃H₂₂O₄, Fig.1.

Table. Effect of ultrasound, microwave and combined MW/US-irradiations on oxidation of beta-linalool with air, temperature – +80°C

Entry v(Linalool) , mol Type of radiation/ Power, W/Run time, h	1 0.045 US/ 350 /5	2 0.045 MW/US/ 450/350 /5	3 0.045 US /450 /1.5	4 0.045 US /350 /1.5	5 0.023 MW/650/1.5	6 0.023 MW/650/5
Conversion of Linalool, %	65.6	44.4	20.8	27.6	11.2	52.4
GC-MS area %						
cis- Linalool oxide (furanoid)	3.8	little	little	little	little	little
2-(5-ethenyl-5- methyloxolan-2- yl)propan-2-yl ethyl carbonate	little	6.4	little	little	little	5.6
(3E)-2,6- dimethylocta-3,7- diene-2,6-diol	3.8	little	little	little	little	little
(2Z)-2,6- dimethylocta-2,7- diene-1,6-diol	21.6	16.0	6.8	9.6	4.0	16.0
(2E)-2,6- dimethylocta-2,7- diene-1,6- diol	13.2	10.4	5.6	7.2	3.2	12.8
2,6-dimethylocta- 1,7-diene-3,6-diol	little	little	little	little	-	-
(5E)-3,7- dimethylocta- 1,5,7-trien-3-ol	17.6	10.8	8.4	10.4	4.0	13.6
1-methyl-4-prop-1- en-2-ylcyclohe- xane-1,2-diol	5.6	0.8	-	little	little	4.4
Sum of GC-MS area % of oxides	3.8	little	little	little	little	little
Sum of GC-MS area % of diols	44.2	27.2	12.4	16.8	7.2	33.2

With growth of temperature from 40 to 80°C linalool conversion sharply increases as at irradiation of MW and so US; data for 80°C are provided in Table. At the same, content of diols in the reaction products also increases to 44.2 and 33.2 GC-MS area%, especially substances **7** and **8**, as well as trienol **10** (Table, Entries 1, 6).

From the US irradiation power of 200-350-450 W, an extreme dependence of the linalool conversion was observed with a maximum at 350 W, respectively, 16.7, 27.6 and 20.8% (Table, Entries 3, 4); data for 200 W are not shown. Under the combined action of MW/US (Table 1, Entry 2),

the linalool conversion, the content of diols and (5E)-3,7-dimethylocta-1,5,7-trien-3-ol were reduced in comparison with the data separately for MW and US irradiation (Table, Entries 1, 2, 6).

In the reaction products no epoxides were found and the content of cis- and trans- linalool oxide (furanoid) was insignificant in contrast to the oxidation reaction without irradiation [5,9]; this is consistent with the fact that the formation of oxides from linalool probably must pass via linalool tertiary hydroperoxide (Linalool-OOH) and then through epoxide [5].

A comparison of the structures of the obtained compounds and linalool (Fig. 1) suggests the possible ways of linalool conversion during its air-oxidation under the influence of microwaves and ultrasounds irradiations; as is known, allylic C–H bonds are about 15% weaker than the C–H bonds in ordinary sp^3 carbon centers and are thus more reactive [10]; the linalool molecule at positions 5, 8 and 9 contains allyl hydrogen atoms, the abstraction of which in the presence of US and MW is likely to be facilitated, ultrasounds and microwaves initiate the formation of radicals. This will lead to an increase in the formation of allyl radicals of linalool; the latter, when interacting with triplet oxygen, form peroxy radicals [2] and then the corresponding hydroperoxides of linalool with different locations of OOH groups, the decomposition of which produces secondary products of linalool oxidation: alcohols, ketone aldehydes [8]. In the reaction products in the highest content there were diols: **7**, (2Z)-2,6-dimethylocta-2,7-diene-1,6-diol $C_{10}H_{18}O_2$ and **8**, (2E)-2,6-dimethylocta-2,7-diene-1,6-diol $C_{10}H_{18}O_2$, also hotrienol i.e. **10**, (5E)-3,7-dimethylocta-1,5,7-trien-3-ol $C_{10}H_{16}O$; the precursor of the formation of these diols, apparently, should be primary linalool hydroperoxide in which the hydroperoxide group of OOH is in position C8, C5. Therefore, during the oxidation of linalool with oxygen of air in the presence of MW and US, C6-C7 carbon-carbon double bond (alkenyl carbon) of beta linalool are primarily activated [8], which facilitates even easier separation of allylic hydrogen atoms at C5 and C8 atoms. In particular, **10**, $C_{10}H_{16}O$ was probably formed in

this way. Apparently, upon irradiation, the activation of both 1,2- and 6,7 carbon double bonds of linalool leads to cyclization and to the formation of **11**, $C_{10}H_{18}O_2$.

Conclusion

The oxidation of terpene alcohol linalool ($C_{10}H_{18}O$) in a stream of pure air under ultrasonic, microwave and combined microwave/ultrasonic irradiations at 40-80°C was studied. The air was taken in excess in comparison with linalool; US and MW irradiations powers varied in the range of 150-650 W; MW and US frequencies were 2450 MHz and 25 kHz, respectively. By air-oxidation of linalool under US and MW irradiations qualitatively the same products are formed; the conversion of linalool is greater when irradiated with ultrasound; with the combined action of US and MW, the conversion and quantitative content of products are significantly reduced. During the air-oxidation of linalool under MW and US irradiations at 40-80°C the monoterpene diols ($C_{10}H_{18}O_2$, (2Z)-2,6-dimethylocta-2,7-diene-1,6-diol, (2E)-2,6-dimethylocta-2,7-diene-1,6-diol) and (5E)-3,7-dimethylocta-1,5,7-trien-3-ol, $C_{10}H_{16}O$ were mainly formed; under US irradiation their content in the reaction products was 40.4 and 17.6 GC/MS area %, respectively. The formation mainly of diols by irradiated air-oxidation of linalool was explained by the supposition about radical mechanism.

The study was carried out under Project #217868 “The new approaches in syntheses of geraniol, nerol and citral” supported by Shota Rustaveli National Science Foundation of Georgia.

ფიზიკური ქიმია

ლინალოლის ჟანგვა ჰაერით ულტრაბგერის და მიკროტალღების დასხივებისას

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**ივანე ჯავახიშვილის თბილისის სახელმწიფო უნივერსიტეტი, პეტრე მელიქიშვილის ფიზიკური და ორგანული ქიმიის ინსტიტუტი, თბილისი, საქართველო

|| მ. ვ. ლომონოსოვის სახელობის მოსკოვის სახელმწიფო უნივერსიტეტი, ქიმიის ფაკულტეტი, კინეტიკის და კატალიზის ლაბორატორია, მოსკოვი, რუსეთის ფედერაცია

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#სან დიეგოს სახელმწიფო უნივერსიტეტი საქართველოში, თბილისი, საქართველო

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გამოკვლეულია ტერპენული მესამეული სპირტის ლინალოლის ჟანგვა 40-80°C ტემპერატურებზე ჭარბი ჰაერის ნაკადში ულტრაბგერისა და მიკროტალღების დასხივებისას. ცდები ტარდებოდა უგამხსნელოდ, გამოიყენებოდა 150-650 W სიმძლავრის და 2450 MHz და 25 kHz სიხშირეების მიკროტალღა და ულტრაბგერა, შესაბამისად. ჟანგვის პროდუქტების ანალიზი ტარდებოდა ქრომატომას-სპექტრომეტრული მეთოდით (Agilent Technologies GC/MS, 7890B/5977A, USA). მიღებული ჟანგვის პროდუქტები ძირითადად შედგება ალილური დიოლებისაგან (C₁₀H₁₈O₂): (3E)-2,6-დიმეთილოქტა-3,7-დიენ-2,6-დიოლი; (2Z)-2,6-დიმეთილოქტა-2,7-დიენ-1,6-დიოლი; (2E)-2,6-დიმეთილოქტა-2,7-დიენ-1,6-დიოლი; 2,6-დიმეთილოქტა-1,7-დიენ-3,6-დიოლი; 1-მეთილ-4-პროპ-1-ენ-2-ილციკლო-ჰექსან-1,2-დიოლი; აგრეთვე მასში არის (3S,5E)-3,7-დიმეთილოქტა-1,5,7-ტრიენ-3-ოლი, C₁₀H₁₈O, ძალიან მცირე რაოდენობით ცის- და ტრანს-ლინალოლ ოქსიდები (ფურანოიდი, C₁₀H₁₈O₂) და 2-(5-ეთენილ-5-მეთილოქსოლან-2-ილ)პროპან-2-ილ ეთილ კარბონატი, C₁₃H₂₂O₄.

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Received September, 2019