# QUANTITATIVE DETERMINATION OF LINALOOL USING THE REACTION OF EPOXIDATION WITH PEROXY DECANOIC ACID

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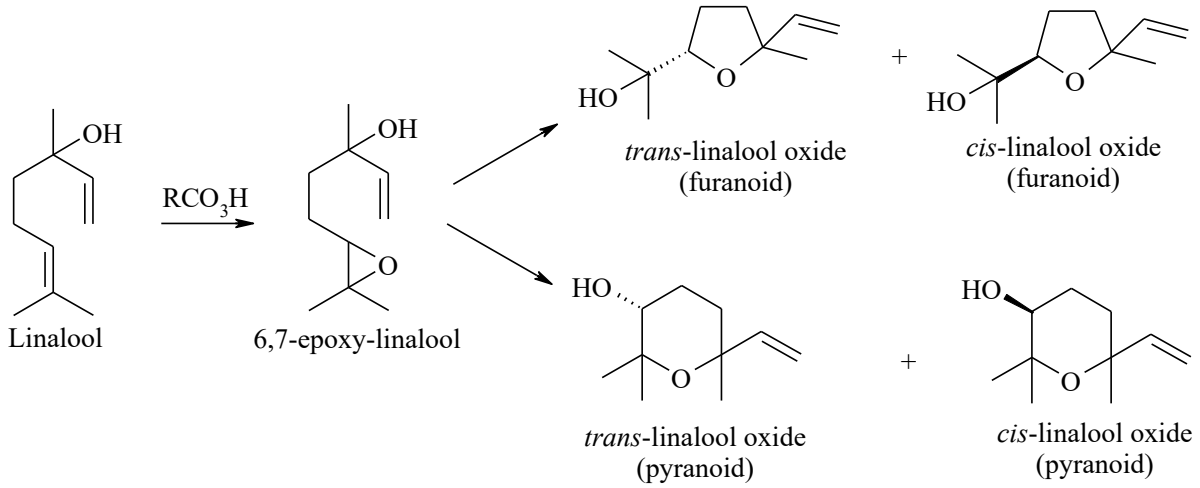
One of the most interesting terpene alcohols found in nature, linalool is also one of the most widely occurring, in its free state and in the form of its esters, in both optical modifications. The oxidation of Linalool with organic peroxy acids has already been discussed [1, 2]. The oxidation of linalool by organic peroxyacids has already been repeatedly discussed in the literature. The reactions of perbenzoic acid and monoperoxyphthalic acid on Linalool have been examined by Prileschaev [3] and Naves and Bachmann [4], the main product being Linalool monoxide. Linalool dioxide may also be formed. Peroxy acid are oxidized the more nucleophilic of the two double bonds contained in the Linalool molecule, i. e. the alkene at the 6,7-position. The monoepoxide formed was very unstable, and rapidly cyclized to form tetrahydrofuran derivative. The cis and trans isomers of this product were both by GLC analysis, and the proton NMR corresponded with that published by Felix et al [5]. The only other possible cyclisation, involved the formation of the tetrahydropyran derivative via the sterically less favored route (Scheme). The oxidation of linalool using *m*-chloroperbenzoic acid at room temperature gave the mixture of 2,2,6-trimethyl-6-vinyl-tetrahydro-pyran-3-ol and 2-(5-methyl-5-vinyl- tetrahydro-furan-2-yl)-propan-2-ol, which cannot be separated [6].




**Scheme** Epoxidation of Linalool with peroxy acid

Modern methods routinely used for determining the composition and quality of essential oils include Gas Chromatography (GC), high performance liquid chromatography (HPLC), Mass Spectrometry (MS) and NMR spectroscopy [7,8]. Chromatographic techniques such as GC and HPLC are used to separate essential oils into their individual constituents so that they can be identified and potentially quantified by a coupled detector such as a MS [9]. The GC technique lends itself to the analysis of essential oils, as it is ideal for the analysis of volatile organic compounds. When used in conjunction with MS and NMR spectroscopy, GC has revolutionized the detection of minor chemical constituents within essential oils. MS looks at the fragmentation patterns of compounds under ionizing conditions, and this information is

used to deduce their structures. NMR elucidates the structures of molecules by examining the environment of specific atoms such as $^{1}$hydrogen and $^{13}$carbon within a molecule. The sensitivity of analytical techniques for organic compounds has increased dramatically over recent years [10, 11].

Furthermore, the development of chiral GC-MS techniques has been found to be a useful approach for the authentication of essential oils [12, 13]. The use of a chiral column in GC enables the analyst to separate enantiomers from one another and determine their unique ratios. The ratio of enantiomers within an essential oil is indicative of its biological origin and thus can provide strong evidence of any adulteration. Chiral GC-MS has been shown to detect lavender oil adulterated with synthetic linalool and linalyl acetate [14-16], lavandin oil [17].

ISO standard 11024 [18, 19] details the GC protocol for obtaining chromatographic profiles of essential oils, detailing the compounds and representative characteristics that can be used to assess oil quality. This requires an authentic reference standard to which unknown oils are assessed against, after chromatographic integration and peak alignment. The approach outlined in the standard requires the use of a skilled analytical chemist, and the integration and comparison between samples can be a time-consuming process if multiple samples from multiple batches are to be analyzed.

One approach to expedite the screening of oils and make them available for sale faster is through the use of data titrimetric chemical analysis.

The present communication reports the use of peroxy decanoic acid (**PDA**) as analytical reagent for the indirect titrimetric determination of Linalool. The proposed method is based on the quantitative oxidation of Linalool with the oxidant in methylene chloride media to the corresponding Linalool monoxide. The excess PCA was iodometry titrated applying either visual end-point detection. To determine the stoichiometry of the reaction, peroxy acid titration of standard solutions was carried out.

Typical kinetic curve obtained for Peroxy decanoic acid-Linalool reaction are shown on the Figure 1.

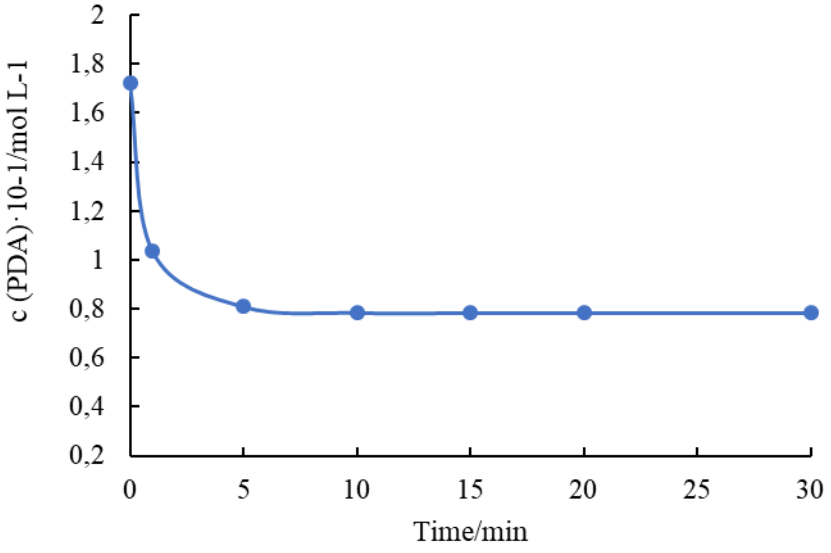



**Fig. 1.** The typical kinetic curve for Peroxy decanoic acid-Linalool reaction.

The required amount of Linalool was dissolved in a known volume of 0.02 mol $L^{-1}$ solution PDA in methylene chloride. After 10 min, the solution was acidified. The excess PDA was iodometry titrated applying visual end-point detection approach.

*Data from quantitative iodometric experiments*.

Reaction stoichiometry: 1 mol of Peroxy decanoic acid is consumed per 1 mol of linalool. The content of the main substance in the substance, *w*. %

$$w = \frac{(V_0 - V_1) \cdot 0{,}1 \cdot K \cdot M \cdot V \cdot 100}{2 \cdot m \cdot 1000} = \frac{(3{,}45 - 1{,}62) \cdot 0{,}1000 \cdot 154{,}24 \cdot 10 \cdot 100}{2 \cdot 0{,}13880 \cdot 1000} = 101{,}7\%.$$

where, $V_0$ is volume of 0,1 mol $L^{-1}$ sodium thiosulphate solution used for titration in the control (without test substance sample) experiment, ml;

$V_1$ is volume of 0.1 mol $L^{-1}$ sodium thiosulfate solution used on titration in the working experiment, ml;

K is correction (conversion factor) to the concentration of the solution with $c(Na_2S_2O_3)$ = = 0.1 mol $L^{-1}$;

V is final volume of solution, ml; 100 - conversion into percent;

*m* is weight of the sample, g;

1000 is conversion into moles; M is molar mass of the substance, g / mol.

$$\text{IV} = \frac{(V_0 - V_1) \cdot 0{,}1 \cdot K \cdot 126{,}93 \cdot V \cdot 100}{m \cdot 1000} = \frac{(3{,}45 - 1{,}62) \cdot 0{,}1000 \cdot 126{,}93 \cdot 10 \cdot 100}{0{,}13880 \cdot 1000} = 167{,}35\%.$$

Iodine value, IV (theor.) = 164.6.

Inverse-concentration anamorphosis of the kinetic curve epoxidation reactions of linalool with peroxoctanoic acid are shown on the Figure 2.

$k_{obs}$ = 3.9 L $mol^{-1}$ $min^{-1}$ (298 K)

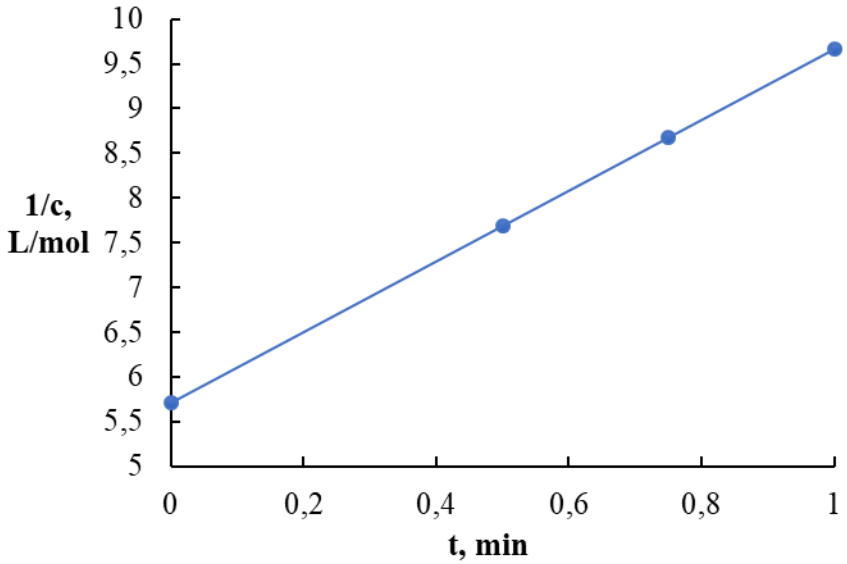



**Fig. 2.** Inverse-concentration anamorphosis of the kinetic curve epoxidation reactions of linalool with peroxoctanoic acid

*Indirect titration.* Add an aliquot (100.0 mg) of the sample in 10 ml methylene chloride a known volume of $1 \cdot 10^{-2}$ M (PDA) solution in a glass-stopper Erlenmeyer Flask. Shake the mixture occasionally and, after 10 min, add 1 ml of 50% acetic acid solution 1 ml of 5%

potassium iodide solution. Titrate the liberated iodine with a $2 \cdot 10^{-2}$ M sodium thiosulfate solution ($V_2$). Carry out a blank experiment in the same manner (V1). Calculate the amount of the Linalool from the equation Linalool (mg) = $[(V_0 - V_1)\ MR]/N$, where $V_0$ is the volume of sodium thiosulfate consumed in the blank titration (ml); $V_1$ is the volume of sodium thiosulfate consumed in the experiment (ml); M is the relative molecular mass of the Linalool; *R* is the molarity of the epoxidizing agent; and *N* is the number of moles of epoxidizing agent per mole of sample.

The advantages of the applied analytical techniques in the determination of Linalool in substance has been presented. The recovery of this analyte in preparation sample ranged from 99.6 to 101.7%. A paired *t*-test showed that all results obtained for Linalool in model solutions and substance, using the proposed procedure and the official procedure respectively, agreed at the 95% confidence level.

**Conclusion**. The kinetics and stoichiometry of the peroxyacid oxidation reaction of linalool in methylene chloride with peroxydecanoic acid have been studied. A method has been developed and the possibility of quantitative determination of the content of the basic substance in linalool samples by the method of inverse iodometric titration using peroxydecanoic acid as an analytical reagent has been shown.

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