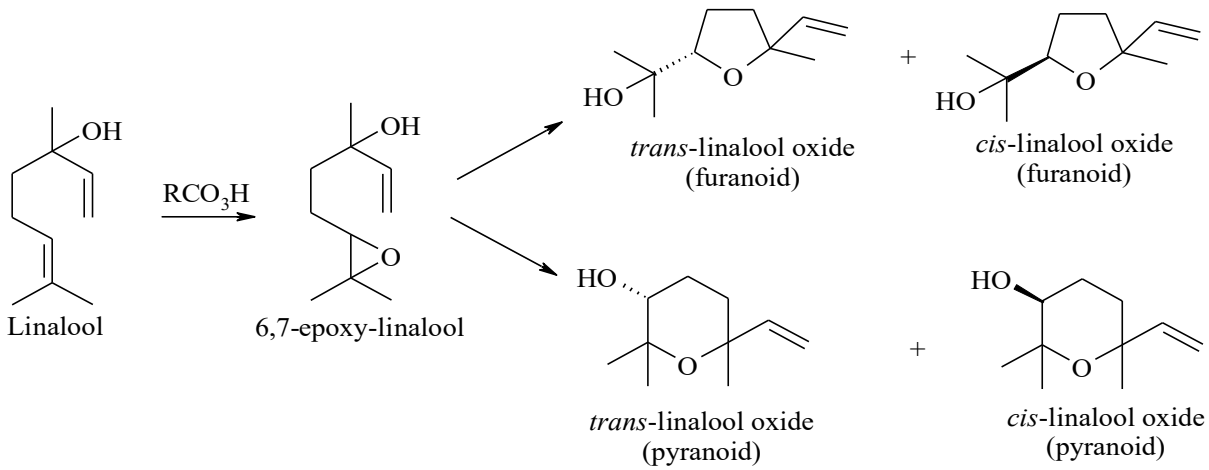
QUANTITATIVE DETERMINATION OF LINALOOL USING THE REACTION OF EPOXIDATION WITH PEROXYDECANOIC ACID

Blazheyevskiy M. Ye., Moroz V.P., Mozgova O.O.
National University of Pharmacy, Kharkiv, Ukraine
blazejowski@ukr.net

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 by organic peroxy acids has already been repeatedly discussed in the literature. The reactions of perbenzoic acid and monoperoxyphthalic acid with Linalool have been examined by Prilezhaev and Naves and Bachmann the main product being Linalool monoxide. Linalool dioxide may also be formed. Peroxy acids oxidize the more nucleophilic of the two double bonds contained in the Linalool molecule, i.e. the alkene at the 6,7-position. The only other possible cyclisation, involved the formation of the tetrahydropyran derivative via the sterically less favoured route (Scheme).



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. 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, lavandin oil ISO standard 11024. 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 peroxydecanoic 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 PDA was iodometry titrated applying either visual end-point detection.

The required amount of Linalool (100-150 mg) was dissolved in a known volume 0.2 mol L^{-1} of PDA in methylene chloride solution. After some time, an aliquot of the solution was acidified. The excess PDA was iodometry titrated applying visual end-point detection approach.

Reaction stoichiometry: 1 mmol of peroxydecanoic acid is consumed per 1 mmol of linalool. To determine the stoichiometry of the reaction, peroxy acid titration of standard solutions was carried out.

As an example, the following are the results on the procedure of indirect titration and of the calculation of the content of the basic substance (*w,* %) and the iodine value of the analyzed sample of Linalool.

$$w = \frac{(V_0 - V_1) \cdot 0.02 \cdot K \cdot M \cdot V \cdot 100}{2 \cdot m \cdot 1000 \cdot V_a} = \frac{(17.25 - 8.23) \cdot 0.02 \cdot 154.24 \cdot 10.00 \cdot 100}{2 \cdot 0.13880 \cdot 1000 \cdot 1.00} = 100.23\%.$$

where, V_0 is the volume of 0.1 mol L^{-1} sodium thiosulfate solution spent on titration in the control (without a portion of the test substance) experiment, ml;

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

K is correction (conversion factor) to the concentration of the solution with ($Na_2S_2O_3$) = 0.02 mol L^{-1};

V is the final volume of the solution, mL; 100 is conversion into percent;

V_a is the aliquot volume of the solution, mL;

m is a sample weight, g;

1000 is conversion into moles; M is a molar mass of the substance, g mol^{-1}.

Iodine Value (IV) is a number of grams of iodine absorbed by 100 g of Linalool:

$$\text{IV} = \frac{(V_0 - V_1) \cdot 0.1 \cdot K \cdot 126{,}93 \cdot V \cdot 100}{m \cdot 1000 \cdot V_a} = \frac{(17.25 - 8.23) \cdot 0.0200 \cdot 126.93 \cdot 10.00 \cdot 100}{0.13880 \cdot 1000 \cdot 1.00} = 164.97$$

Iodine Value (theor.) = 164.6 number of grams of iodine absorbed by 100 g of oil.

The method is developed and the possibility of quantitative determination of the content of the main substance in the substance Linalool by iodometric titration of peroxydecanoic acid is shown. 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 100.7 % (*n*=5; *P*=0.95). RSD ≤1.9%. 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.