Entrainer Effects on the Phase Behavior of Origanum Oil/CO_2 System at Sub/Supercritical Conditions

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Abstract – The effect of ethanol as entrainer on the relative equilibrium distributions of 14 characteristic components of origanum oil *(Origanum Munituflorum)* in the oil and sub/supercritical CO_2 phases is investigated at 25, 35, 45 and 55 ^oC and at constant pressure of 80 atm. Terpenes are most sensitive to temperature change since they are the components with highest volatilities. The addition of 5 wt% ethanol as entrainer increases the solubility of the more polar components of the oil in the solvent phase and therefore enhances the separation of these components from the less polar components.

Introduction

Essential oils are the volatile oils derived from plants. They are mixtures of organic compounds that carry the essential odor and flavor of the parent plant. Like other essential oils, origanum oil and its fractions find use as raw materials in industries such as pharmaceutical, food and cosmetics. Therefore, the extraction and isolation of essential oils from plants and the concentration of their valuable compounds/fractions are of industrial importance.

Supercritical Fluid Extraction (SFE) of essential oils from plants, as well as fractionation of the extracted oils to desired products have received great interest [1]. With its low critical temperature (31 ^oC) and moderate critical pressure (73 atm) CO_2 is an exceptional non-toxic solvent, which permits extraction and fractionation operations on gentle essential oils to be carried out at relatively mild conditions. At pressures near the critical point, a moderate increase in temperature can induce a large decrease in fluid density resulting in a decrease in solute solubility. This is known as the retrograde behavior. SFE may make use of the retrograde behavior of the supercritical-fluid systems, when such behavior is encountered.

In industrial practice a multicomponent extract may be separated into its fractions either by applying phase separations at sub/supercritical pressures and temperatures, or via using a multistage column at similar conditions. In both of these cases the basic data necessary are the relative distribution of the components between the dense-gas and the liquid phases.

This research involves experimental studies to determine the relative equilibrium distributions of the 14 major origanum-oil *(Origanum Munituflorum)* components in the oil and sub/supercritical CO_2 phases at 25, 35, 45 and 55 ^oC and 80 atm, as well as the effect of the addition of ethanol as entrainer on the relative equilibrium distributions of the origanum-oil components.

Experimental Setup

The experimental setup, which has been reported in detail in some previous work [2,3] consists of a high-pressure equilibrium cell with sampling system, an agitation mechanism and a water bath.

The equilibrium cell, shown in Fig.1 has 255.5 cm^3 effective volume (12 cm height, 6 cm ID, 8 cm OD). It is a bolted-closure type high-pressure vessel manufactured of 316 SS. A Teflon O-ring gasket between the head and the vessel ensures sealing of the cell to prevent gas leakage at high pressures. The pressure in the cell is measured by a pressure gauge with a measurement range of 0-280 kg/cm^2 (Pakkens Instruments).

A motor-driven pulley, connected to a metal cradle immersed in a constant temperature bath, carries out the agitation of the cell. The temperature of the bath is kept within ±0.1 ^oC by a thermostat (Heto Instruments). The equilibrium cell is placed horizontally and is covered completely with water in the bath. The mixing of the dense-gas phase and the liquid origanum oil in the equilibrium cell is accomplished by the horizontal movements of the cradle at a rate of 43 swings per minute.

The exterior part of the equilibrium cell contains sampling lines and the valve system. As seen in Fig.1, the dense-gas sampling is achieved by three high-pressure on-off valves V1, V2, and V3 (1/4 in ID, two-way ball valves) that are connected to each other with the stainless-steel tubing (1/4 in).

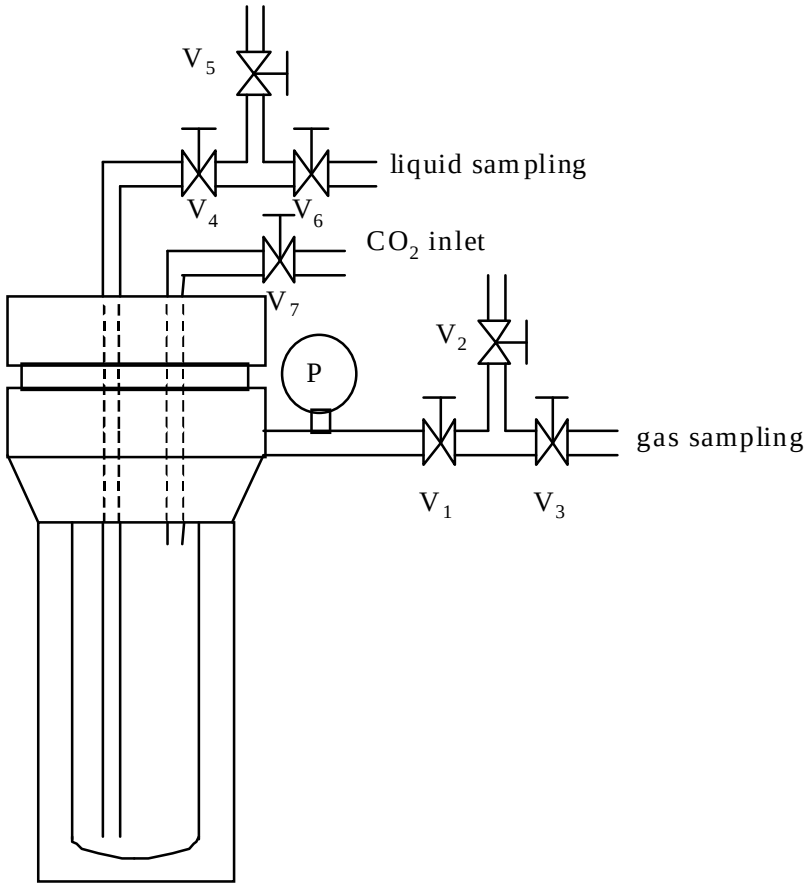


Figure 1: The Equilibrium Cell.

The dense-gas is trapped in the line between V1, V2 and V3. In the liquid-phase sampling, a similar line with three high-pressure on-off valves V4, V5, and V6 (1/4 in), and stainless steel tubing (1/8 in) are used to trap the liquid sample. The liquid-sampling line extends through the interior of the equilibrium cell to the bottom to ensure the successful sampling from the liquid phase. Valves V3 and V6 are used to release the samples to sampling bottles, while the valves V2 and V5 are opened to wash out the precipitated solutes inside the lines with ethanol. The liquid CO_2 is fed through a pumping line (1/4 in) with the high-pressure on-off valve V7 (1/4 in).

Materials and Methods

The material used for this study was origanum oil derived from the *Origanum Munituflorum* plant grown in the wild in the Mediterranean region of Turkey and supplied by Altes Ltd. Co., Ýstanbul. CO_2 (99.7% pure), in cylinders equipped with dip tubes, was supplied by Habaþ Inc., Ýstanbul.

In the experiments, a previously determined amount, i.e., 20 ml of origanum oil was put into the equilibrium cell, the cell lid was closed and the bolts tightened. The cell was then placed horizontally onto the cradle and in the water bath that had been heated to the desired temperature. It is important to preheat the equilibrium cell to water-bath temperature in order to prevent the pressure of the cell to exceed the pre-determined value for the particular experiment after pumping CO_2 into the cell. Then, liquid CO_2 was pumped into the cell while the temperature of the water bath was controlled within $\pm 0.1\ ^{o}C$ of the desired value.

After the desired pressure was attained in the cell, the cradle motor was switched on to start the agitation of the equilibrium cell. The cell was shaken for 90 min to allow the phases to reach equilibrium. After 90 min, the motor was switched off and the cell was left motionless for another 90 min to eliminate possible entrainment of the oil droplets in the dense-gas phase and to ensure the separation of the two phases. At the end of this stationary period, the cell contents were assumed to be at thermodynamic equilibrium at the temperature and pressure of the particular experiment. More details on the basics of the experiments maybe found in [3].

Before sampling, the cell was taken out from the bath. The sampling was carried out in the traps between the three valves for each phase separately. The dense-gas-phase samples were trapped by opening the valve V1 for 15 seconds while keeping the valves V2 and V3 closed. Then the dense-gas sample was released by opening the valve V3 slowly and the gas was let through a plastic tubing into the glass sampling bottle. The bottles were previously filled with 2 ml of ethanol and with glass beads in order to increase the contact time and surface area between the gas sample and the trapping solvent ethanol. After the entire gas sample trapped was passed through the ethanol, the sampling line was washed with 1.5 ml of ethanol injected from the valve V2 in order to recover any oil remaining in the sampling line. After the gas sample was taken, the same procedure was repeated for the line trap in between the valves V4, V5, and V6 to recover the liquid sample. However, this time, the valve V4 was opened and closed very quickly, as the liquid sample tends to flow to the sampling bottle in larger amounts as compared to the amount of the gas sample. Then, the valve V6 was opened to release the pressure inside the line after the sampling bottle was positioned under the sampling line.

In the experiments done using ethanol as entrainer to investigate the entrainer effects on the phase behavior of the system, 5.0 wt% or 2.5 wt% ethanol was added to the oil during charging the equilibrium cell, keeping the rest of the procedure the same as in the first part.

The analyses of the original origanum oil and the experimental samples were performed using a GC/MS (HP 5890/5971, Carbowax 20M capillary column). A total of 12 experiments, including four to check reproducibility, were performed at 25, 35, 45, and 55 ^{o}C at 80 atm.

Results and Discussion

Table.1 summarizes the classification and analysis of the origanum-oil components in the original oil.

Component	Classification	Area %
α-thujene	MT	5.24
camphene	MT	1.25
β-pinene	MT	0.45
β-myrcene	MT	3.21
phellandrene	MT	0.52
α-terpinene	MT	2.88
limonene	MT	0.61
cineole	OX	1.32
γ-terpinene	MT	10.96
p-cymene	MT	11.50
linalool	AL	8.82
caryophyllene	ST	4.16
endo-borneol	AL	4.90
carvacrol	PH	44.19
Total MTs %:		36.62
Total NMTs %:		63.38

Table 1: The key components of the origanum oil.

To interpret the relative distribution of the components between the phases, a relative-distribution ratio (R_i) is used. The relative-distribution ratio of each phase, R_i, is defined as [2,3]:

$$R_i = \frac{C_i^{eq}}{C_i^{o}} \qquad i = 1,...,n \quad (i \neq CO_2) \tag{1}$$

In this relation C_i^{eq} (T,P) denotes the normalized solvent-free concentration (area % in the GC/MS analysis) of the origanum-oil component *i*, in either phase, and the symbol C_i^{o} is used for the normalized concentration of the same component in the feed (original oil).

The value of R is important in determining the amount of a component in the dense-gas and liquid phases. The R values greater than one means that the component concentration (or, the monoterpene (MT) or non-monoterpene (NMT) fraction) is more in the dense-gas phase than in the oil fed to the equilibrium cell. The R values equal to one means that the component concentration is the same in the dense-gas phase and in the oil fed to the equilibrium cell. The R values less than one means that the component concentration is less in the dense-gas phase than in the equilibrium cell. Here, R_y will refer to gas-phase relative distribution of the components, and R_x will refer to liquid-phase relative distribution of the components.

Depending on temperature, at constant pressure, the R_y values of the components show different behavior. As the temperature is decreased, the density of the solvent phase increases. This increase in the density of the solvent phase is proportional to the increase in its solvent power.

For this reason, it can be stated that, as the temperature is decreased the components are dissolved more and more in the solvent phase, therefore the R_y values of the components converge to one. On the other hand, as the temperature is increased, the solvent power decreases resulting from the decrease in CO_2 density, and the R_y values of the components deviate from unity leading to the result that the component concentration is more in the oil obtained from the solvent phase than in the feed, but this increase in the R_y values differ for each component. This fact is evident in Fig.3 and Fig.4. The increases in the R_y values are observed to be significant in more volatile components whereas the R_y values of the less volatile components such as *carvacrol* and *caryophyllene* do not exhibit a considerable change with respect to the change in temperature. Nevertheless, as the temperature is increased, a decline in the relative distributions of these components is observed. The value of R_y for *carvacrol* is near to, but less than one, showing that *carvacrol* preferentially remains in the liquid phase. Furthermore, studying Fig.1 in more detail, it can be seen that most of the components lie in the range $0<R_y<3$, and only a few components are seen with R_y values around 3.5 and 4. Similar argument can be made for the components in the liquid phase. In Fig.2, the components in the liquid phase have R_x values between 0 and 3. The R_x values again decrease as the temperature is decreased.

In the second part of the study, the experiments are carried out at the same temperatures and at 80 atm constant pressure, but this time ethanol is added as entrainer to the oil charged to the equilibrium cell in order to investigate the effects of this polar entrainer. In Fig.2 and Fig.3, the analyses of the data obtained from these experiments are included in order to make a comparison between the experiments done with and without the entrainer. Since ethanol is a polar co-solvent and therefore increases the overall polarity of the solvent phase, the polar components in the origanum oil are more easily dissolved in the gas phase. So theoretically, the R_y values of the polar components such as *linalool*, *endoborneol*, *caryophyllene*, and *carvacrol* should be higher in the gas samples obtained in the experiments with the entrainer. However, when Fig.2 and Fig.3 are studied in more detail, it can be seen that when 5 wt% of ethanol is added to origanum oil, the gas- and liquid-phase data obtained without entrainer do not differ considerably from the data obtained with the entrainer. One of the possible reasons for this is the excess amount of ethanol added to oil. Excessive amounts of ethanol may have attracted not only the more polar components in the oil but also the less polar components and therefore may have failed the purpose of solubilizing more of the more polar NMT components and less of the less polar MT components. In order to check this assertion, experiments are carried out with 2.5 wt% ethanol. The data obtained from these experiments, which are included in Fig.2 and Fig.3 as well, prove that if 2.5 wt% ethanol is added to the system, the more polar NMT components are selectively solubilized by the solvent. Therefore, the R_y values of the more polar components increase with the addition of 2.5 wt% ethanol (R_x values of these components decrease as can be seen in Fig.3).

Conclusions

The results obtained are informative towards the determination of optimum operating conditions for supercritical fractionation and investigation of the effects of entrainer on the phase behavior of origanum-oil/CO_2 system at sub/supercritical conditions. Comparing the data obtained from the experiments with and without ethanol, it may be concluded that the addition of an entrainer to an oil-/solvent-phase system enhances the separation between components with lower and higher polarities by increasing the polarity of the dense-gas solvent, if the entrainer-to-oil ratio does not exceed an effectiveness limit, after which the addition of entrainer shows little or no effect, which is about 2.5 wt% ethanol in our study.

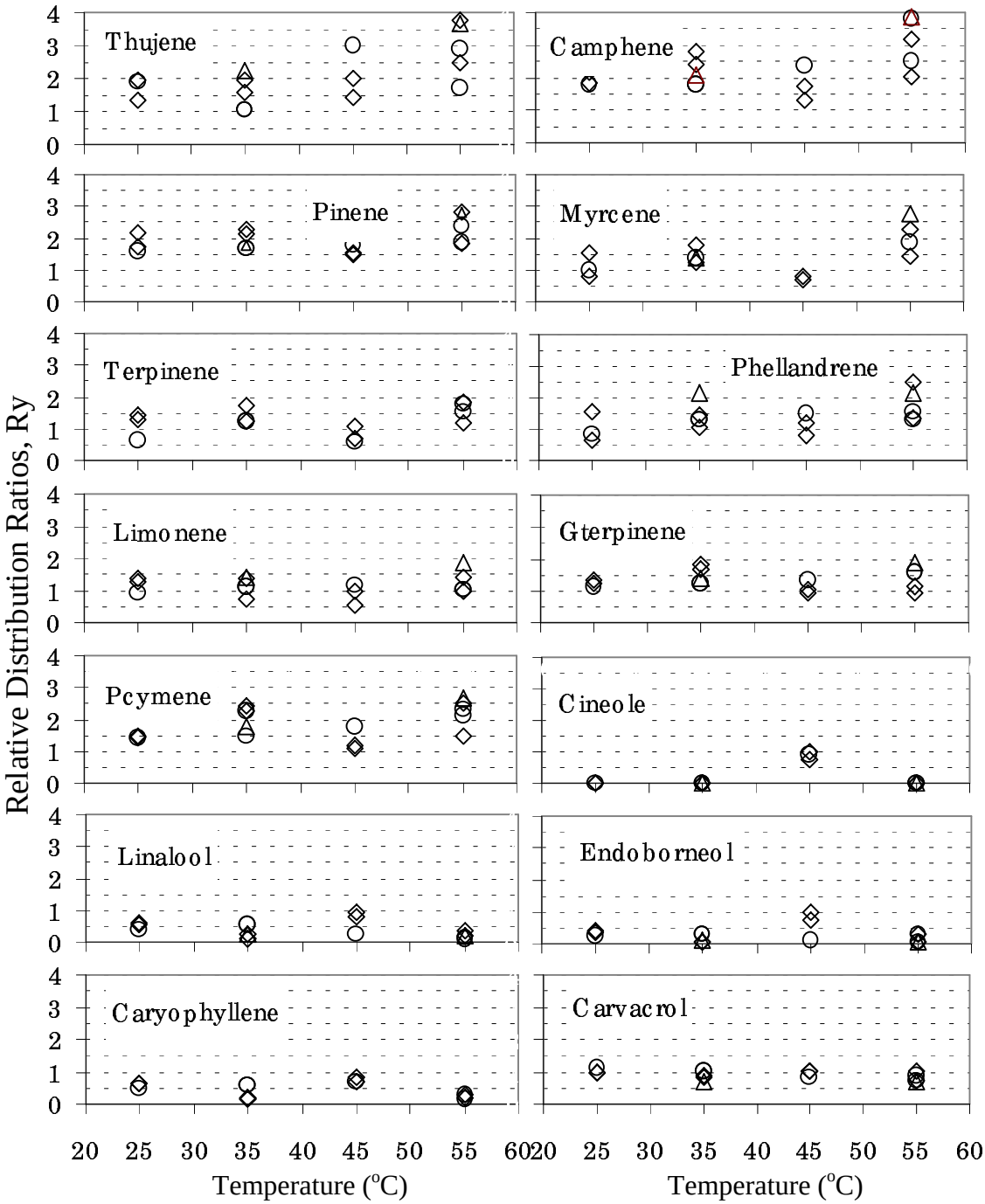


Figure 2: Effect of ethanol entrainer on the relative distribution of the key components in the dense-gas phase, ◊: without ethanol, ϒ: 5% ethanol, Δ: 2.5% ethanol.

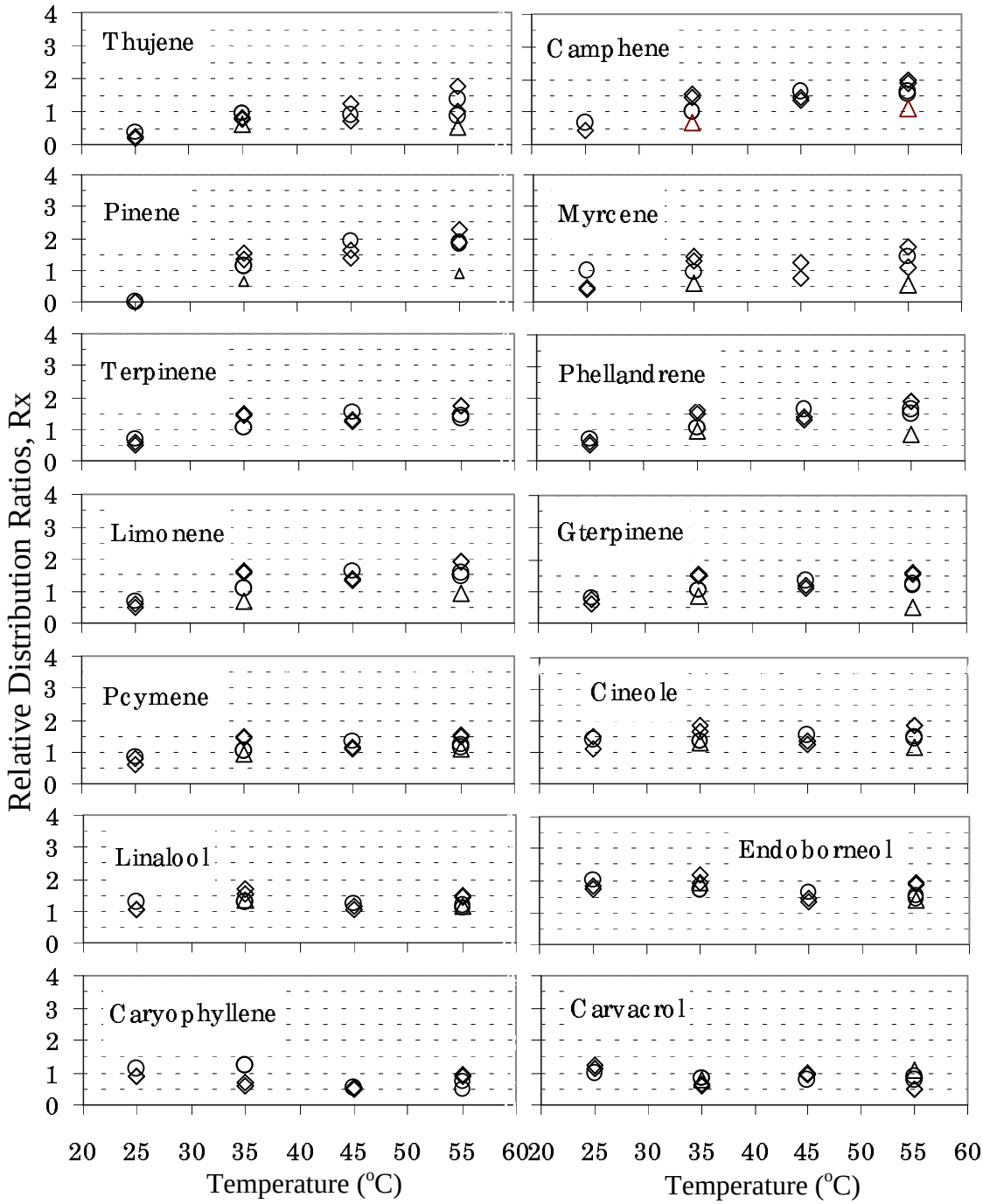


Figure 3: Effect of ethanol entrainer on the relative distribution of the key components in the liquid phase, ◊: without ethanol, ϒ: 5% ethanol, Δ: 2.5% ethanol.

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Nomenclature

AL	alcohol
MT	monoterpene
NMT	non-monoterpene
OX	oxygenated
PH	phenolic
ST	sesquiterpene

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