α-Terpineol from Hydration of Crude Sulfate Turpentine Oil

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Hydration of α-pinene under various conditions was studied and compared with the literature. Optimal reaction conditions have been established for the hydration of α-pinene and crude turpentine oil in the absence of catalyst and using a low volume of acetone. A detailed reaction product analysis is reported. The main hydration product, α-terpineol, was obtained at a yield of 67 wt % of the initial α-pinene by reacting with 15% aqueous sulfuric acid and an excess of acetone in an oil bath heated to 80−85 °C over the course of 4 h. A progressive transformation of α-terpineol to 4-(2-hydroxypropyl)-1-methylcyclohexanol (1,8-terpine) takes place as the hydration time exceeds 4 h. A crude turpentine oil sample was also hydrated under conditions similar to those of α-pinene. The α-terpineol yield was 77 wt % of the initial α-pinene in the crude turpentine oil. The chemical analysis of the crude turpentine oil before and after hydration was carried out, and the distribution of the products was discussed.

Keywords: *Hydration; α-pinene; α-terpineol; essential oil; turpentine; yield; emulsifier*

INTRODUCTION

Crude sulfate turpentine is one of the kraft pulping process byproducts of pine wood. It is a cheap material with limited applications and contains malodorous organic sulfur compounds, elimination of which is costly. Many perfume chemicals are produced from α-pinene and β-pinene, the main constituents of turpentine which is extracted directly from pine wood distillation. It has been known for many years that through hydration in diluted mineral acids, α-pinene is converted into a complex mixture of monocyclic terpenes, terpene alcohols, and hydrocarbons. Some authors have studied the composition of the reaction products, while others have concentrated on some particular products for their smelling properties (*1*, *2*). Furthermore, several authors investigated the transformation of terpenes into their corresponding alcohols, such as α-terpineol which is used in perfumes (*3*) and in mineral flotation (*4*). Those methods, however, are less practical, particularly in a large-scale production unit due to either a low level of conversion, long reaction time, or utilization of catalyst and solvents with high boiling points which incur additional operating costs due to the catalyst regeneration or solvent recovery.

The main objective of this work was to develop an efficient hydration reaction with a short reaction time for the production of α-terpineol from kraft turpentine. The hydrated turpentine oil, also called "synthetic pine oil", finds its use in mineral flotation, in processing textiles, and as a solvent, odorant, and bactericide. In this work, a commercial α-pinene sample was initially hydrated and the reaction yield was optimized. Then, a sample of crude sulfate turpentine oil was hydrated. The

yield and composition of the reaction products are reported.

Catalytic Hydrations. In 1947, Mosher (*5*) studied the product distribution of acid-catalyzed α-pinene hydration products. The author brought to the fore the treatment of α-pinene with 1-chloro-4-naphthalenesulfonic acid which led to the formation of β-pinene, limonene, terpinolene, and α-terpinene. Several years later, in 1971, Williams and Whittaker (*2*) investigated the rearrangements of acid-catalyzed hydration reactions of α-pinene and β-pinene in aqueous acetic acid and in anhydrous acetic acid. They compared the composition of modified products of α- and β-pinene reactions, with either perchloric acid (0.0947 N in 10% aqueous acetic acid at 25 °C) or sulfuric acid (0.0982 N in 10% aqueous acetic acid at 25 °C). They observed notable differences. The maximum yield was obtained after 6 h with both acids. However, the yield was 55% with perchloric acid compared with 34% with sulfuric acid. They showed that the rate constants for the conversion of α- and β-pinene in 10% aqueous acetic acid, containing 0.0982 N sulfuric acid at 25 °C, are lower for β-pinene than for α-pinene. They concluded that the change from anhydrous to 10% aqueous acetic acid greatly reduced the difference between the product distributions. The direct hydration of olefins using a strong cation-exchange resin catalyst (*6*), which is especially suitable for lower alkenes such as propylene, resulted in a limited conversion of the olefins of less than 5%.

The hydration of α-pinene can also be accomplished with zeolites. Zeolites may have the potential to improve selectivity. However, the kinetic size of the α-pinene molecule restricts the use of zeolites to large pores such as Y, β, and mordenite type zeolites (i.e., 12-membered rings, with a pore diameter in the range of 7−7.5 Å). Nomura et al. (*7*) used various zeolites (CA-Y, US-Y, NA-X, and ferrierite) during the hydration of very dilute aqueous solutions of α-pinene to α-terpineol. The highest selectivity to α-terpineol was obtained using ferrier-

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ite (69% yield over the course of 117 h at 90−110 °C). van der Waal et al. (*8*) used a new zeolite, named H-beta, as a catalyst for the hydration and/or isomerization of α-pinene. This reaction is fast and in the presence of water leads to monocyclic terpenes and alcohols with 48 wt % α-terpineol as the main component. The authors brought to the fore the formation of a new product named α-terpinyl acetone upon isomerization of α-pinene followed by a reaction with ketone in pure acetone, butanone, or cyclohexanone.

A direct hydration of terpenic olefin such as α-pinene with 99% conversion and a 72% yield of α-terpineol has been reported by Nigam et al. (*9*) using a 2-propanol/water mixture as a solvent at a reaction temperature of 80−83 °C over the course of 20 h.

Hydration in the Presence and Absence of an Emulsifying Agent. In a patent claimed by Charwath (*10*), a C_{18} fatty alcohol has been used to hydrate a crude turpentine oil. The reaction time was 24 h, but no yield was reported. Several years later, another patent has been claimed by Reiner (*11*) in which α-terpineol was prepared by hydration of a turpentine oil using an aqueous solution of sulfuric and phosphoric acids in the presence of ethoxylated octylphenol. An α-terpineol yield of 57.8 wt % was reported on the basis of the α-pinene content of the initial turpentine oil. Bibicheva et al. (*12*) focused on a method for a one-step synthesis of terpineol in the absence of an emulsifying agent. In this method, the reaction was carried out with sulfuric acid, acetone, and water. The α-pinene hydration products were as follows: 21−26% α-terpineol, 1−2% β-terpineol, and 2−4% γ-terpineol (the three main products).

EXPERIMENTAL PROCEDURES

Hydration of α-Pinene. A mixture containing 2 g of α-pinene purchased from Aldrich Canada and 4 mL of a 15% (v/v) aqueous solution of sulfuric acid with an excess of acetone (∼25 mL) was refluxed in an oil bath at 80−85 °C. The solution was kept under constant agitation during reflux. The hydration experiment was carried out over the course of 10 h. A sample was taken, diluted, and analyzed for α-terpineol content at every 30 min time interval during the hydration. The mixture was neutralized to pH 7 with a 5% aqueous NaOH solution after reflux and then diluted to 100 mL with acetone prior to the analysis. The product analysis revealed a 6−10% decrease in the yield of α-terpineol when the sample was not neutralized prior to the analysis.

Hydration of Turpentine Oil. The turpentine oil was kindly supplied in March 1999 by Donohue Inc. (St. Félicien, PQ). The experiment was carried out using the same procedure as that used for the commercial α-pinene. GC/MS analyses of the initial sample indicated the presence of 52 wt % α-pinene (Table 1). Methanethiol and dimethyl disulfide were the main sulfur compounds found in the crude turpentine oil sample.

Analysis. The analysis was performed in a Hewlett-Packard model 5890 gas chromatograph. The separation was performed on a 30 m × 0.25 mm (inside diameter) HP-5MS fused silica capillary column with a 0.25 nm film of crossed-linked 5% phenyl methyl silicone. The GC oven temperature was held at 50 °C for 2 min, then increased to 200 °C at a rate of 5 °C/min, and then increased to 290 °C at a rate of 30 °C/min. The oven temperature was maintained at the final temperature for 10 min. The injector temperature was set at 290 °C with split mode (1/20 split ratio). Helium was used as the carrier gas at a flow rate of 1 mL/min. The end of the column was directly introduced into the ion source of a Hewlett-Packard model 5970 mass selective detector operated in the electron impact ionization mode. The typical operating conditions for the mass spectrometer were as follows: transfer line temperature of 270 °C, ion source temperature of 250 °C, and

Table 1. Composition of Crude Turpentine Oil before and after Hydration for 4 h[a]

compound	wt %	
	before	after
α-pinene	52.0	nd
β-pinene	11.4	nd
3-carene	4.2	4.4
terpinolene	nd	2.7
α-terpineol	3.9	40.1
limonene	3.3	7.9
eucalyptol	nd	0.3
β-terpineol	1.4	1.1
γ-terpineol	nd	1.1
γ-terpinene	1.0	11.7
camphene	0.8	2.5
fenchyl alcohol	0.7	6.3
β-myrcene	0.6	nd
camphor	0.4	nd
1-methyl-4-isopropylbenzene	0.3	nd
1,7,7-trimethyltricycloheptane	0.2	0.2
borneol	0.1	5.8
1,8-terpine	nd	2.6
α-terpinene	0.1	1.4
other organic compounds	nq	nq
total	80.4	89.7

[a] nd, not determined; nq, not quantified.

Table 2. Standard Compounds and Their Relative Response Factors to Anthracene

compound	response factor[a]	standard deviation
α-pinene	2.34	0.12
3-carene	2.14	0.07
limonene	2.33	0.09
camphene	2.29	0.07
α-terpineol	2.59	0.14

[a] Average of seven analyses.

an electron energy of 70 eV. Data acquisition was carried out with a PC base G1034C chemstation software and a NBS mass spectra library data. The mass range of m/z 30−350 was scanned every 0.8 s. The computerized match was manually evaluated to ensure the quality of identification. Identification of selected target compounds was also confirmed by matching their mass spectra and retention times with those of the standard compounds. One hundred microliters of a solution containing 131.5 mg of anthracene in 50 mL of ethyl acetate was added as an internal standard to the sample solutions whose volume was 2 mL prior to GC/MS analyses. Five solutions of standard compounds from Aldrich Canada (Table 2) with concentrations of 100, 200, 300, 400, and 500 ppm were prepared in ethyl acetate. Their response factors with respect to anthracene were calculated. The results are given in Table 2. The response factor of alcohols other than α-terpineol in Table 1 was assumed to be 2.59 (similar to that of α-terpineol), and that of the other hydrocarbons was assumed to be an average of four values in Table 2, i.e., 2.34, 2.14, 2.33, and 2.29.

RESULTS AND DISCUSSION

Hydration of α-Pinene. Panels a and b of Figure 1 are chromatograms of commercial α-pinene before hydration and a spectrum of the products obtained after hydration for 4 h, respectively. The chromatograms obtained at various time intervals indicate that there is a definite evolution of certain products over time. One notes the reduction in α-pinene content after reaction for 0.5−3 h. A complete conversion was reached after reaction for 4 h. However, the different experiments indicated that the rate of α-pinene hydration is related to the temperature of the oil bath. When the temperature of the oil bath was maintained at 70−75 °C, the
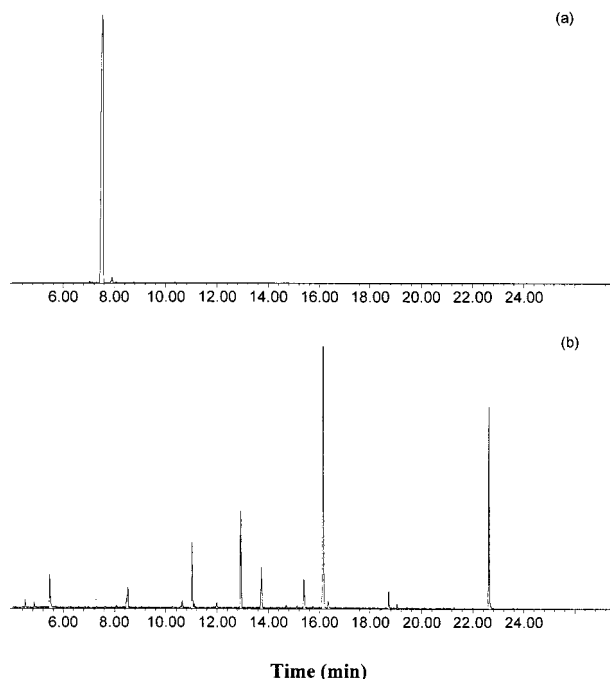
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Figure 1. Chemical composition of the commercial α-pinene: (a) before hydration and (b) after hydration.
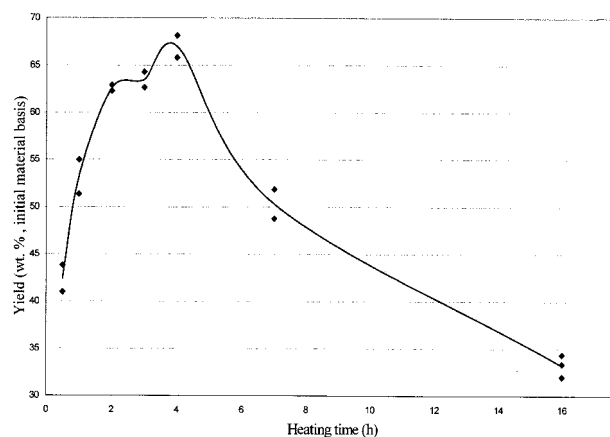

Figure 2. Yield of α-terpineol as a function of heating time.

rate of hydrolysis was significantly lower than when the oil bath temperature was set at 80−85 °C. The hydration product distribution was also found to be dependent on the reaction temperature. It is therefore important to maintain a relatively constant oil bath temperature during the experiments. Earlier, Vital et al. (*13*) reported the kinetic data of α-pinene hydration to terpene in an isobutanol/aqueous sulfuric acid solution. Their investigation was based on the rate of the hydration reaction. They observed a slow reaction with an order of 0.81 after adjustments at low temperatures which is not surprising due to the nonhomogeneous reaction mixture. As they increased the reaction temperature to ca. 100 °C, they obtained first-order kinetics. They reported that the chemical reaction takes place only in the aqueous phase.

The quantity of α-terpineol formed during the course of the reaction was determined using anthracene as the internal standard, and the yield of conversion of α-pinene to α-terpineol was calculated. The results are summarized in Figure 2. The data are the result of two parallel experiments. Not more than 4% absolute error is attributed to both experimental and GC analysis.

Table 3. Yield of the α-Pinene Hydration Products as a Function of Heating Time[a]

compound	yield based on the initial amount of α-pinene (mol %)			
	3 h	4 h	7 h	16 h
β-pinene	1.8	nd	nd	nd
α-pinene	1.6	nd	nd	nd
camphene	3.2	2.5	2.3	1.4
1-methyl-4-(1-methylethyl)-7-oxabicyclo[2.2.1]heptane	nd	nd	nd	1.5
terpinolene	nd	nd	nd	2.5
limonene	8.4	8.3	5.0	5.0
eucalyptol	nd	nd	2.3	1.8
α-terpinene	nd	1.0	1.1	1.6
γ-terpinene	12.5	14.2	16.5	10.4
fenchyl alcohol	6.1	6.5	8.2	5.2
borneol	5.3	5.2	7.6	4.5
α-terpineol	57.8	58.0	45.8	29.5
γ-terpineol	nd	1.8	2.8	3.8
1,8-terpine	3.0	2.5	6.3	7.1
total	99.7	98.80	97.90	74.30

[a] nd, not determined.

Derivatization of α-terpineol prior to the analysis is expected to reduce the analytical error by increasing the chromatographic response. Table 2 shows that the α-terpineol experiences a relatively lower response with respect to anthracene as an internal standard. Figure 2 indicates that the conversion reaches a maximum at 4 h when α-pinene is fully converted to α-terpineol and the rate is nearly zero. The unusual "saddle-like shape" of the α-terpineol formation between 2 and 3 h is presumably due to the predominance of the isomerization reactions of α-pinene to limonene and terpinene. Monitoring of the formation of limonene and terpinene between 0 and 3 h will shed further light on that hypothesis. It is known that α-pinene passes through a number of intermediate equilibrium reactions to form α-terpineol and other isomeric compounds. This may also explain the retardation of α-terpineol formation within the reaction period of 2−3 h. At 4 h, both isomerization and α-terpineol formation are completed and α-pinene is fully converted.

Other experiments with a heating time of >4 h were carried out to determine the evolution of α-terpineol and the other reaction products. The GC/MS analyses indicated the formation of a number of compounds when the heating time was greater than 4 h. In addition, a few of those compounds, such as α- and β-terpinene, γ-terpineol, and 1,8-terpine, were formed in large amounts at a longer heating time. The formation of products derived from the secondary reactions of hydration was favored with prolonged reaction time. The GC/MS results for the reaction products are listed in Table 3. The difference from 100 in Table 3 indicates the presence of compounds which have not been identified or detected due to their low concentration or/and poor matching quality with the standard compounds. The rate of formation of 1,8-terpine was lower than that of α-terpineol after hydrolysis for 4 h. The yield of α-terpineol decreased with the formation of more 1,8-terpine after 4 h as shown in Figure 3. Acid-catalyzed hydration of α-pinene in aqueous 95% acetone (v/v) containing 0.075 N sulfuric acid at 75 °C has been reported by Williams and Whittaker (*14*). Their product analysis indicates a conversion yield to α-terpineol lower than what is reported in this paper. Their results showed more isomeric products of α-pinene than the hydrated products. Under the conditions described in
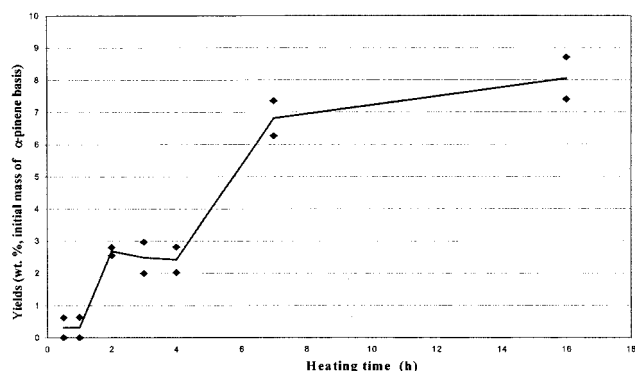
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Figure 3. Relative amount of 1,8-terpine as a function of heating time in α-pinene.

this paper, the main reaction product is α-terpineol. Approximately 26 mol % of a mixture of isomeric forms of α-pinene is also produced, including camphene, limonene, α-terpinene, and γ-terpinene (see Table 3).

α-Terpineol is modified by acid to other products, mainly 1,8-terpine. α-Terpineol (**1**) is subjected to an electrophile attack on the double bond by the H⁺ ions of the solvated acidic protons acid, forming a cation (**2**) which then yields 1,8-terpine (**3**). However, a parallel reaction can also take place, involving the coupling of H⁺ ions with the OH group of α-terpineol to form a cation (**4**) which can lead to an intermediate (**5**).
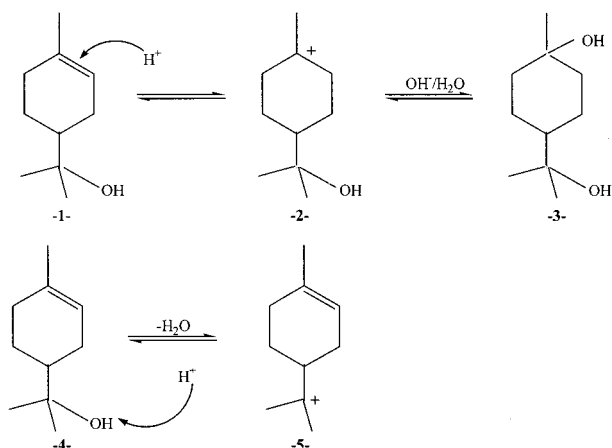
Cation **5** is the source of a variety of secondary reactions. Several other unidentified products appeared after 16 h of heating which are not listed in Table 3. Like α-terpineol, limonene is formed in high yield after hydration for 4 h. The quantity of α-terpineol was highly reduced after heating for 4 h, forming mainly 1,8-terpine and γ-terpineol. The quantity of limonene was also significantly reduced.

Lower reaction temperatures and acid concentrations reduce the extent of the conversion of α-pinene to α-terpineol and initiate the isomerization reactions of α-pinene.

Hydration in the Presence of an Emulsifier. During the course of the different experiments, it was noted that the good homogeneity of the initial mixture greatly influenced the yield of α-terpineol and its reproducibility. We thus decided to determine whether the use of an emulsifier would improve the yield.

In a first series of experiments, oleyl alcohol was tested using the same operating conditions as those described previously in an excess of acetone with an

Table 4. Comparison of the Yields (%) of α-Terpineol after Hydration for 4 h Carried out with and without Emulsifier

without emulsifier	with emulsifier
58.14	50.91
60.17	49.03
59.16[a]	49.97[a]

[a] Average.

Table 5. Yield of α-Terpineol as a Function of Heating Time for the Hydration of α-Pinene in the Presence of an Emulsifier

heating time (h)	α-terpineol yield (%)
20	27.10
	27.05
24	37.60

Table 6. Yield (wt %) of α-Terpineol after Hydration for 4 h with Turpentine Oil and α-Pinene[a]

turpentine oil	α-pinene
75.5	66.4
77.2	68.1

[a] The values for weight percent are based on the initial mass of α-pinene.
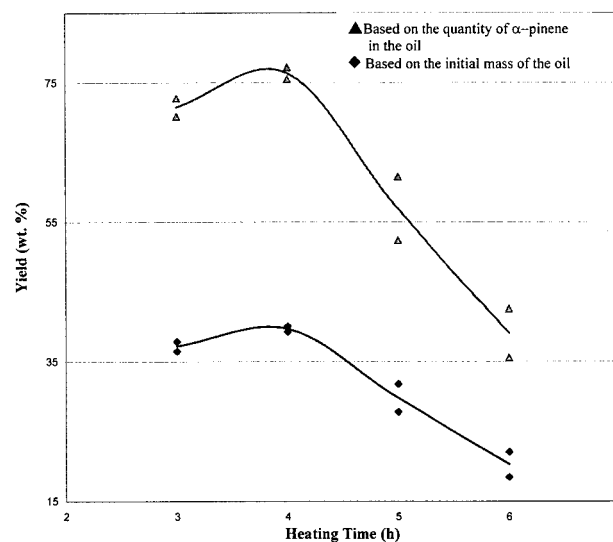

Figure 4. Relative amount of α-terpineol produced as a function of heating time in turpentine oil.

addition of a few drops of the emulsifying agent. For the same heating time (4 h), the yields that were obtained were not better than when the reactions were carried out without an emulsifier, which seems to contradict other reports found in the literature (Table 4). However, it is possible that the excess of acetone and oleyl alcohol, which both have the same homogenization role in the mixture, is preventing to some extent the hydration of α-pinene. A second series of experiments was thus carried out using much less acetone in the hydration reactions. For this series of experiments, the following mixture was used: 6 g of α-pinene, 2.5 mL of 3 N H_2SO_4, 15 mL of acetone, and 0.1 g of oleyl alcohol. Table 5 lists the results obtained after reaction for 20 and 24 h. The results were not as good as expected. An increase in the quantity of α-terpineol formation was noted throughout the temperature range. However, the yields were lower than those obtained using a procedure without an emulsifier. Thus, it could be concluded that the presence of oleyl alcohol does not facilitate the

formation of α-terpineol. It would be interesting to see whether other types of emulsifiers could lead to better results than those obtained with an excess of acetone, i.e., whether there is a compound which could favor the formation of α-terpineol, as opposed to the secondary reaction and isomerization products.

Crude Turpentine Oil. Turpentine oil is a mixture of several terpenes, in particular, α-pinene, camphene, and limonene (Table 2). A series of tests were carried out at hydration times of 3−6 h. The maximum yield of α-terpineol was reached after reaction for 4 h. The hydration experiment was exactly the same as that carried out for the commercial α-pinene. The results obtained during the hydration are summarized in Table 6 and are plotted in Figure 4. The yields were calculated using two different methods. In the first method, the percentage of α-terpineol is expressed with respect to the total mass of initial turpentine. In the second method, the percentage of α-terpineol formed is expressed with respect to the quantity of α-pinene contained in the initial turpentine oil (considering that the amount of α-pinene in this oil was 52%).

Figure 4 indicates that the maximum yield of α-terpineol is obtained after hydrolysis of crude turpentine oil for 4 h, similar to that of the commercial α-pinene. However, a comparison of the α-terpineol yield obtained with the turpentine oil and the commercial α-pinene for the same hydration reaction time indicates some differences. Williams and Wittaker (*2*) reported that limonene and β-pinene also lead to the formation of α-terpineol in the presence of acid. The data, however, indicate that the overall limonene content of the turpentine oil was increased by hydration rather than by transformation into α-terpineol.

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