The Oxidation of Emulsified 1-*p*-Menthene with Molecular Oxygen

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1-*p*-Menthene prepared by hydrogenating purified *d*-limonene has been emulsified in water and oxidized at temperatures between 65 and 80° without any catalyst and at 10° with catalyst present.

Under the former conditions the oxidation of 1-*p*-menthene took place at position 6 while under the latter conditions it took place at positions 3 and 6. The hydroperoxides formed, 1-*p*-menthene-3-hydroperoxide and 1-*p*-menthene-6-hydroperoxide, were found to have the *trans* configuration.

The refractive index n_D^{25} of *trans*-carvotanacetol was found to be 1.4736. This alcohol underwent rearrangement to the *cis* form in both acid and alkaline media. The refractive index n_D^{25} of the resulting *cis*-carvotanacetol was 1.4772.

On chromic acid oxidation, both the *trans* and *cis* forms of carvotanacetol were converted into carvotanacetone ($n_D^{25} = 1.4785$). The infrared absorption spectrum of carvotanacetone was recorded. The infrared spectrum of the piperitone ($n_D^{25} = 1.4825$) derived from 1-*p*-menthene-3-hydroperoxide was identical with that reported by Le Fèvre *et al.* for the compound.

In all stages of the investigation the micro sorption method developed by Blohm proved very useful. With this method it was possible to separate, for example, the *trans* and *cis* forms of carvotanacetol from each other.

When unsaturated cyclic hydrocarbons are oxidized with molecular oxygen, the oxygen usually attacks the carbon atom or atoms in the alpha positions relative to the double bond.¹ When the oxidation is photosensitized, the double bond is shifted at the same time.² In both cases the compounds first formed are hydroperoxides. The photosensitized oxidations will not be discussed in this publication.

Because the oxidation of 1-*p*-menthene with molecular oxygen has not been reported before, the oxidation of a number of compounds similar in structure to 1-*p*-menthene will be first briefly examined. In the oxidation of limonene³⁻⁷ the point of attack is primarily position 6 although according

Fig. 1. Sorptograms. I, pomgranate oil; II, product isolated by steam distillation; III, hydrogenated product.

Fig. 2. Sorptograms. IV, initial fraction 1; V–VIII, fractions 2–5.

to Eschinazi⁶ addition to position 3 also occurs to a slight extent. Fushizaki *et al.*⁸ found that carbon 3 is attacked in the oxidation of terpinolene. The products of oxidation of 1-*p*-methylcyclohexene have indicated that both carbons 3 and 6 are attacked^{9–12}. However, Cook¹³ has reported that the oxidation occurs almost solely at carbon 3. He performed the oxidation at 70° with iron phthalocyanine as catalyst.

The results reported in the literature lead one to conclude that the oxidation of 1-*p*-menthene by molecular oxygen will involve the methylene groups in the alpha positions relative to the double bond, *i.e.* positions 3 and 6. The main purpose of the present study was to determine whether the oxidation takes place at one or both of these positions. To decide this, 1-*p*-menthene was emulsified in water and oxidized with molecular oxygen both with and without catalyst present and the reaction products or their derivatives identified. In addition to customary methods, the micro sorption method of Blohm¹⁴ was used to separate the terpene alcohols and ketones from one another before identification.

Preparation of 1-*p*-menthene. 1-*p*-Menthene was prepared by hydrogenating *d*-limonene isolated from French pomgranate oil (Roure-Bertrand Fils, Grasse). According to Igolen *et al.*¹⁵, pomgranate oil contains over 90 % *d*-limonene. The high *d*-limonene content of the oil used is shown by the sorptogram I (Fig. 1). The oil was first subjected to steam distillation. A part of the minor components passed over in the first fractions and a part remained in the distillation residue. In this and in subsequent stages the products

were protected by a carbon dioxide atmosphere. The distillate was separated from the condensed water and dried with sodium wire at room temperature. The refractive index n_D^{25} of the dried distillate was 1.47021, and its specific rotation $[\alpha]_D^{25} = 97.5'$. The refractive indices of the fractions on the plateau of its sorptogram II (Fig. 1) were the same, $n_D^{25} = 1.47056$, as those of the fractions on the plateau of sorptogram I. Widmark¹⁶ has reported for pure *d*-limonene a refractive index n_D^{25} of 1.4703.

The *d*-limonene fractions were hydrogenated^{17,18} in absolute alcohol with Raney nickel as catalyst. The hydrogenation of *d*-limonene to 1-*p*-menthene proceeded fairly rapidly, but the hydrogenation of the latter to *p*-menthane took place much more slowly. Since it is difficult to separate *d*-limonene and 1-*p*-menthene by fractional distillation, whereas 1-*p*-menthene and *p*-menthane are readily separated, the hydrogenation was continued until the *d*-limonene had been completely hydrogenated. The progress of the reaction could be easily followed by recording sorptograms of samples taken during the reaction. As the unsaturation of *d*-limonene decreased, the refractive index of the reaction mixture decreased rapidly and at the same time the adsorption on the sorptogram column. Owing to this, the first sections of the sorptograms gave the refractive index of *p*-menthane, then that of 1-*p*-menthene, and finally that of *d*-limonene. The hydrogenation was terminated when the peak for *d*-limonene had disappeared from the sorptogram. Water, one tenth of the volume of the hydrogenated mixture, was added, whereupon the hydrogenation products rose to the surface and the product containing oxygen remained in solution¹⁹. The upper layer was washed with water and its sorptogram (Fig. 1, III, $n_D^{25} = 1.4533$) recorded.

The products of hydrogenation were fractionally distilled in a packed column with 10 theoretical plates. The distillate was separated into the fractions shown in Table 1. From the sorptograms IV–VIII for these fractions the 1-*p*-menthene contents were estimated by assuming the fractions to contain only 1-*p*-menthene, $n_D^{25} = 1.45445$, and *p*-menthane, $n_D^{25} = 1.4372$ ($n_D^{20} = 1.4395$ ¹⁸).

Table 1. Fractional distillation of hydrogenated product.

Fraction No.	B.p. (°C) at 13 mm Hg	Weight in grams	n_D^{25}	% 1- <i>p</i> -menthene
1	—60.5	53	1.44696	57
2	60.5—61	59	1.45123	81
3	61—61.5	205	1.45355	95
4	61.5—62	212	1.45441	100
5	62	78	1.45442	100
residue		15		

Specific rotation of fraction 4: $[\alpha]_D^{25} = 98.5'$.

The oxidation of 1-p-menthene with molecular oxygen. The oxidations with and without catalyst were conducted by passing oxygen into an emulsion of 1-*p*-menthene in water. The results are presented in Fig. 3 and Table 2.

The previously employed emulsion oxidation procedure²¹ was slightly modified. To effect a vigorous mixing a vibrator mixer (Vibro-Mischer, A. G. für Chemie Apparatebau, Zürich) was employed. This made possible the use of a thermostat. As in the earlier experiments²¹, a 0.5 % aqueous solution of sodium stearate, to which sodium carbonate had been added to give the pH indicated, was first used as emulsifying medium (Expts. Nos. 1–6). A 0.3 % sodium stearate solution proved to be more effective than the 0.5 % solution at the temperatures employed (cf. expts. Nos. 2 and 5, Fig. 3).

As shown by the curves for expts. Nos. 1, 2 and 3 in Fig. 3, the rate of oxygen absorption rose rapidly as the temperature was increased. The oxidation was interrupted in these experiments as soon as 10 % of the oxygen required

Table 2. Oxidation of 1-*p*-menthene.

Expt. No.	t°C	Emulsion 1- <i>p</i> -menthene	Water ml	Emulsifier in water % ^b	Time min.	Oxygen ml ^a	Peroxide formed, %	% of oxygen consumed in peroxide	Initial pH	Final pH
1	65	20	40	0.5	325	270	8.7	72	10.0	10.0
2	70	20	40	0.5	250	270	8.6	70	10.0	10.0
3	80	20	40	0.5	70	270	8.8	72	10.0	7.9
4 ^c	70	20	40	0.5	320	510	14.5	64	10.0	7.1
5	70	20	40	0.3	285	510	15.0	66	10.1	7.8
6	80	20	40	0.5	175	520	15.0	65	10.0	6.7
7	70	60	60	0.3	440		14.4		10.1	7.9
8	10	50	100	^d	1 165	2 235	13.7	36	9.2	7.6

^a Oxygen (N.T.P.) introduced.

^b Emulsifier sodium stearate except in Expt. No. 8.

^c 1-*p*-Menthene previously treated with 8 % sodium hydroxide solution ²⁰.

^d Emulsifier 1 % Teepol (Shell Chem. Corp.; dry matter 40 %).

to oxidize 1-*p*-menthene to 1-*p*-menthene-hydroperoxide had been consumed. In these experiments the hydroperoxide values of the reaction products were equal, which indicates that the rate of oxidation and the rate of hydroperoxide decomposition increased in the same degree with increasing temperature. About 70 % of the oxygen added was found in the hydroperoxides formed in these experiments. When the reaction time was prolonged, the hydroperoxide content of the product increased, but at the same time the proportion of added oxygen that was bound as hydroperoxide decreased.

When the product of expt. No. 2 was stored at room temperature for four months, the hydroperoxide content fell gradually from 8.6 to 5.6 %.

In expt. No. 8 cobalt resinate was employed as catalyst and the temperature was only 10°. Since even a dilute sodium stearate solution becomes viscous at this temperature, sodium secondary alkyl sulphate (Teepol 710) was

Fig. 3. Oxygen consumption as a function of time.

Fig. 4. Sorptograms. IX, expts. Nos. 1, 3-6, "ketone mixture"; X, expt. No. 7, "alcohol mixture"; XI, synthetic carvotanacetone.

used as emulsifier. The rate of oxidation was nearly as great in this experiment as in expt. No. 2 at 70°. No induction period was observed as in the other experiments. Despite the low temperature, the hydroperoxide decomposed more rapidly than in the other experiments in which the temperatures were much higher. The higher rate of decomposition was evidently due to the presence of the catalyst.

Identification of oxidation products

The oxygen compounds formed in the emulsion oxidation were for the most part hydroperoxides in all experiments except No. 8. The other products formed were mainly alcohols, ketones and polymers.

The hydroperoxides in the reaction products were reduced in sodium sulphide²² and sodium sulphite solutions²³. The reduced oxidation products were separated from 1-*p*-menthene by passing their solution in petroleum ether through a column packed with silica gel (BDH, for chromatographic analysis) as proposed by Kirchner *et al.*²⁴ When this separation was performed on the oxidation product of expt. No. 8, a part of the oxidized material passed through the silica gel layer; this fraction was recovered subsequently by passing it a second time through a silica gel column. The oxygen-containing compounds were retained quantitatively by the silica gel and the sorptogram of the product that passed through the column revealed it to be pure 1-*p*-menthene. The oxidation products were eluted from the silica gel with anhydrous ether. The results are shown in Table 3.

Table 3. Reduced oxidation products after separation from 1-*p*-menthene.

Expt. No.	1, 3-6	7	8	
Oxidation products	8.0 g	8.3 g	8.9 g	(2.8 g ^a)
Ketone content		12 %	34 %	

^a Oxidation product recovered in the second elution.

The reduced oxidation products, which mainly consisted of alcohols, were oxidized to the corresponding ketones with chromic acid in acetic acid solution^{25,26} (Table 4). The ketones in the resulting mixtures were determined gravimetrically as their dinitrophenylhydrazones according to Scholtens²⁷ (Tables 3 and 4).

Table 4. Ketone mixtures.

Expt. No.	1, 3-6	7	8	
Weight of mixture	8.0 g	1.4 g	6.4 g	(2.2 g ^a)
Steam distilled product ^b	5.7 g	0.8 g	4.1 g	(1.1 g)
Ketone content	60 %	ca. 80 %	ca. 90 %	

^a See subnote to Table 3.

^b Amount removed by steam distillation from products of chromic acid oxidation.

Oxidations without added catalyst. Expts. Nos. 1, 3-7. The ketones obtained in expts. 1 and 3-6 were combined and converted into a dinitrophenylhydrazone which melted at 187-190° after three crystallizations from ethanol. With synthesized carvotanacetone-2,4-dinitrophenylhydrazone (m.p. 191-192°^{28,29}), this derivative gave a mixed melting point of 187-191°. Since the

solubility of piperitone dinitrophenylhydrazone in ethanol was much greater than that of the corresponding derivative of carvotanacetone, the original dinitrophenylhydrazone precipitate was fractionated by chromatography according to Montes³⁰. The dinitrophenylhydrazone passed through the adsorbent as one zone, from which it was concluded that no appreciable amounts of 1-*p*-menthene-3-hydroperoxide corresponding to piperitone, but only 1-*p*-menthene-6-hydroperoxide corresponding to carvotanacetone, had been formed in the oxidation.

The sorptogram IX of the same ketone mixture is shown in Fig. 4. Two different sections, one (A) showing a minimum and the other (B) a maximum, are evident in the sorptogram.

The fractions of section A gave a copious dinitrophenylhydrazone precipitate which, after two crystallizations from ethanol, melted at 189–191°. The refractive index, $n_D^{25} = 1.4736$, of section A is much lower than the refractive index, $n_D^{25} = 1.47855$, of pure carvotanacetone (sorptogram XI, Fig. 4). Despite this large difference, the fractions giving section A can be concluded to have been impure carvotanacetone.

The fractions of section B, which yielded only a negligible amount of a dinitrophenylhydrazone, were concluded to be carvotanacetol that had not been oxidized to carvotanacetone in the chromic acid treatment²⁵. On the other hand, the reduced oxidation product of expt. No. 7 gave the sorptogram X (Fig. 4), the refractive index of which was, however, much lower than the refractive index of section B in sorptogram IX. The only explanation for the difference between the sorptograms appeared to be that the alcohol (carvotanacetol) that had not been converted into ketone by chromic acid had undergone isomerization to another alcohol which had an appreciably higher refractive index than the alcohol formed in the reduction of the original hydroperoxide.

To decide this, the reduced oxidation product of expt. No. 7 was isomerized by boiling in glacial acetic acid. The resulting product gave the sorptogram XII in Fig. 5. This sorptogram consists of three separate sections. The refractive index of the first highest plateau was almost the same as that of section B in sorptogram IX. The refractive index of the third section or the second highest plateau was identical with that of sorptogram X for the reduced product of expt. No. 7. It is hence obvious that only a part of the alcohols had been isomerized. The section of the sorptogram between the two plateaus was evidently due to the acetate of one of the alcohols, as indicated by the strong odour of carvotanacetol acetate given off by the fractions.

All of the isomerized product was saponified with ethanolic potassium hydroxide, and the product liberated distilled with steam. The distilled alcohol gave the sorptogram XIII of Fig. 5. After a gradual rise the sorptogram levelled off, and the refractive index of this section was close to the refractive index of the isomerized carvotanacetol that was assumed to be present. It is thus obvious that not only were the esters saponified but also the unisomerized alcohol underwent isomerization. The refractive index in the main section of the sorptogram XIII for the distilled and isomerized alcohol was close to that for synthesized carvotanacetol³¹, $n_D^{25} = 1.4772$ (Sorptogram XIV, Fig. 6).

Fig. 5. X, expt. No. 7, "alcohol mixture"; XII, expt. No. 7, isomerized product; XIII, expt. No. 7, saponified product.

Fig. 6. XI, synthetic carvotanacetone; XIV, synthetic carvotanacetol; XV, expt. No. 7, "ketone mixture" prepared after saponification.

The saponified product contained 10 % ketone. This ketone evidently increased the refractive index of carvotanacetol, and since the ketone precedes the alcohol, as in sorptogram IX, the highest part in the sorptogram XIII is due to carvotanacetone.

Under the conditions where the isomerization was carried out ²⁹, carvotanacetol is dehydrated to some extent and forms menthadienes. These hydrocarbons appear in the first fractions of the sorptograms (e.g. XII and XIII) and lower the refractive index. After the isomerized and saponified product was oxidized with chromic acid and isolated by steam distillation, it gave the sorptogram XV (Fig. 6) which shows first a high peak and then falls close to the refractive index of carvotanacetone (n_D^{25} for synthesized carvotanacetone ³¹ was 1.4785; sorptogram XI, Fig. 6). The refractive index, $n_D^{25} = 1.4875$, at the peak in sorptogram XV is very close to the refractive index, $n_D^{25} = 1.4883$, of *p*-cymene ³². The fractions giving the peak had the odour of *p*-cymene. The *p*-cymene may have resulted from the oxidation of the menthadienes by chromic acid. It is obvious that for this reason there is a gradual decrease before the refractive index of the ketone is reached in all the sorptograms (IX, XV, XVII and XIX) of the products of the chromic acid oxidations.

According to the above, the alcohol with the lower refractive index is formed when the hydroperoxide formed in the emulsion oxidation is reduced, while the alcohol with the higher refractive index results from the isomerization of this alcohol. Synthesized carvotanacetol has the same refractive index as the isomerized alcohol. Hence, since the alcohols both yield carvotanacetone on oxidation with chromic acid, they are carvotanacetols.

According to the rule of Auwers-Skita ³³, the alcohol with the higher refractive index must be the *cis* form. On the other hand, Gastambide ³⁴ has stated that the sterically more hindered form, in this case the *cis* form, is less strongly adsorbed. Consequently the alcohol with the higher refractive index first appearing in the sorptogram XII was *cis*-carvotanacetol. The synthesized carvotanacetol is hence also the *cis* form. However, the carvotanacetol obtained by reducing the oxidation product was more strongly adsorbed than the

preceding and had a lower refractive index and was hence *trans*-carvotanacetol. From this it may be deduced that the main product of the oxidation under the chosen conditions was *trans*-1-*p*-menthene-6-hydroperoxide. This conclusion is confirmed by the nature of the oxidation products of certain terpenes, which products have been shown to have the *trans* configuration^{22,35}.

Oxidation at low temperature in the presence of catalyst. Expt. No. 8. The main part of the reduced oxidation products of this experiment contained 34 % ketone (Table 3). The dinitrophenylhydrazone of the ketone melted at 190–192° after two crystallizations from ethanol, which indicated that the ketone was carvotanacetone. The reduced product of expt. No. 8 gave the sorptogram XVI, which differed completely from the sorptogram X of the corresponding product of expt. No. 7. Certain observations at the time of the experiment and later led to the conclusion that the sorptograms XVI had been formed by partly separated fractions consisting of carvotanacetone, *trans*-piperitol, *trans*-carvotanacetol and piperitone, in this order.

The product of the chromic acid oxidation of the main product of expt. No. 8 (Table 4) gave the sorptogram XVII. In this sorptogram a very high initial peak is followed by a sharp minimum and a fairly high, broad maximum. The minimum is evidently due to carvotanacetone. The mean refractive index of the fractions contributing to the initial peak, $n_D^{25} = 1.4818$, is close to the refractive index of piperitone ($n_D^{20} = 1.4848$ ³⁶; $n_D^{25} = 1.4823$). In addition, these fractions smelled strongly of piperitone.

This product of chromic acid oxidation of the main fraction was distilled in a spinning band column with 25 theoretical plates. The fractions shown in Table 5 were obtained.

Table 5. The distillation of the main product of expt. No. 8 after chromic acid oxidation.

Fraction	$t^\circ\text{C}$ at 3.4 mm Hg	ml	n_D^{25}
1	78.5–79.5	1.0	1.47787
2	—80.5	0.8	1.48082
3	—82.5	0.7	1.48190
4	82.5	0.1	1.48212
residue		0.8

Fig. 7. XVI, expt. No. 8, "alcohol mixture"; XVII, expt. No. 8, "ketone mixture".

Fig. 8. XVIII, expt. No. 8, ketone fraction 1; XIX–XX, expt. No. 8, ketone fractions 2 and 3.

Fig. 9. Infrared spectrum of synthesized carvotanacetone.

The fractions 1, 2 and 3 yielded the sorptograms XVIII, XIX and XX (Fig. 8). The refractive index n_D^{25} of the horizontal section of the sorptogram XVIII was 1.4785, from which it was concluded that fraction 1 consisted mainly of carvotanacetone. The refractive index, $n_D^{25} = 1.4825$, of sorptogram XX suggested that the fraction 3 was almost pure piperitone. Fraction 2 evidently contained both these compounds.

The 2,4-dinitrophenylhydrazone prepared from fraction 3 melted at 113–116° after crystallization from an ethanol-ethyl acetate mixture. The corresponding derivative of piperitone has been reported³⁷ to melt at 116°.

The high yield of piperitone suggests that the oxidation at a low temperature with catalyst present involves addition to position 6, but also to position 3 to a considerable extent.

Infrared spectra

A 30- μ l sample was taken from the middle fractions of sorptogram XX and its infrared spectrum recorded. This spectrum was identical with the spectrum recorded for piperitone by Le Fèvre *et al.*³⁸

An infrared spectrum was also recorded for a sample from the middle fractions of synthetic carvotanacetone giving the sorptogram X. Since the infrared spectrum for carvotanacetone was not found in the literature, the recorded spectrum (Fig. 9) was compared with the Raman spectrum for the compound³⁹. The two spectra for carvotanacetone were found to conform well with each other.

The infrared spectrum obtained for piperitone was also found to agree well with the Raman spectrum of this compound⁴⁰.

Micro sorption method

Blohm's micro sorption method¹⁴ was employed in a slightly modified form. Whereas Blohm and Widmark employed sorptograms only in the analysis of hydrocarbons^{14,16,32,41}, the method was found in this study very suitable also for liquid alcohols and ketones. After the present work had been completed, Widmark published sorptograms for various liquid compounds including carvotanacetone⁴². The refractive index he obtained for

carvotanacetone, $n_D^{25} = 1.4782$, deviates slightly from the value, $n_D^{25} = 1.47855$, obtained in this work.

Commercially available silica gel (BDH, for chromatographic analysis) proved to be a suitable adsorbent. The sieve fraction passing through 200 mesh was employed. The sorptogram tube chosen after some experimentation was a capillary tube 150 cm long with an inner diameter of 1.5 mm. The fractions were collected into capillary tubes 0.76 mm in inner diameter (15–20 tubes). The volumes of the fractions were obtained by measuring the lengths of the liquid columns in the calibrated capillary tubes. In the sorptogram plots the abscissa is the cumulative length of the liquid column of the fractions (10 cm corresponds to 46.5 μ l).

For the recording of each sorptogram an accurately measured 0.20-ml or 0.25-ml volume of the sample was taken. The sample volume was transferred to the top of the column with an injection syringe of 0.5-ml capacity with a scale graduated in 0.01-ml divisions. By using a needle of suitable length the sample could be added so that none of it adhered to the upper walls of the column. After the sample had penetrated into the column packing, alcohol was added from a side tube.

The pressure applied to the column varied from 1.5 to 4.5 atmospheres. Depending on the pressure and the nature of the sample, the passage of the sample through the column took from 3 to 5 h. The oxygen-containing terpenes are more viscous than the hydrocarbons and hence required higher pressures. The passage of synthetic carvotanacetol through the column took over 10 h under a pressure of 4 atm.

The refractive indices of the fractions were measured to the fifth decimal with an immersion refractometer (Eintauch-Refraktometer Nr. 67130, Carl Zeiss, Jena). The light source was a sodium lamp. When the refractive indices were measured the temperature was maintained at $25 \pm 0.05^\circ\text{C}$ with a thermostat (Colora, Ultrathermostat NB-26093).

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