mixture was poured into water, filtered and dissolved in a minimum of ethyl alcohol and treated with Norite. Final recrystallization from ligroin gave a fine needle-like product melting at 151–152°. *Anal.* Calcd. for $C_{22}H_{21}NO$: N, 4.45. Found: N, 4.34, 4.40. Bromination of this derivative in chloroform solution yielded a product, m. p. 184–186°. *Anal.* Calcd. for $C_{22}H_{20}ONBr$: N, 3.55. Found: N, 3.84.

The benzoyl derivative was prepared by warming 2.0 g. of the product with 4 ml. of benzoyl chloride. Upon crystallization from a ligroin–acetone mixture a colorless product was obtained, m. p. 188.0–188.4°. *Anal.* Calcd. for $C_{27}H_{20}ON$: N, 3.71. Found: N, 3.65.

For further characterization, 5 g. of the diphenylmethyl-*o*-toluidine sulfate was dissolved in 50 ml. of glacial acetic acid and 3 ml. of sulfuric acid, cooled to 30° and diazotized by the slow addition of 4 ml. of amyl nitrite. A portion of the diazotized solution was poured into boiling water, then allowed to cool and extracted with two 50-ml. portions of ether. Upon evaporation of the ether the resulting oil was converted to its methyl ether, 2 methyl-4-diphenylmethylanisole, m. p. 75.8°. This gave a mixed m. p. of 75° with the identical material m. p. 74–76° previously prepared in the *o*-cresol series.[2] A second portion of the diazotized solution was treated with zinc dust in ethyl alcohol, replacing the original amino group with hydrogen. The product melted at 61.5° and was shown to agree by mixed melting point with the product made by direct syntheses.[1b]

Characterization of Product IV.—The acetyl derivative of the disubstituted product IV was prepared in a manner analogous to the preparation of the monosubstituted product. The colorless crystals melted at 189–189.5°. *Anal.* Calcd. for $C_{35}H_{31}ON$: N, 2.91. Found: N, 3.27.

The benzoyl derivative was prepared as described above and melted at 232–233°. *Anal.* Calcd. for $C_{40}H_{33}ON$: N, 2.58. Found: N, 2.85.

The disubstituted product IV was diazotized as above and poured into boiling water. Upon cooling, 2 g. of the dark brown solid was acetylated by warming with 10 ml. of acetic anhydride and a trace of sulfuric acid. After reaction, a yellow tarry mass was obtained which was recrystallized from alcohol yielding a colorless crystalline product, m. p. 142–143°. No melting point depression was observed when this material was mixed with O-acetyl-2-methyl-4,6-bis-(diphenylmethyl)-phenol as previously prepared.[2]

Summary

1. The rearrangement of N-diphenylmethyl-*o*-toluidine or the direct reaction of diphenylcarbinol with *o*-toluidine yields products with one and two diphenylmethyl radicals in the nucleus which is analogous to comparable reactions in the *o*-cresol series.

2. An intermolecular mechanism is demonstrated, since a para rearrangement takes place; equal amounts of the disubstituted product and *o*-toluidine are produced and an actual migration of the diphenylmethyl radical from the nitrogen to an *o*-cresol nucleus was observed.

DURHAM, N. H. RECEIVED MARCH 9, 1950

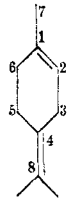
[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

Oxidation of Terpenes with Molecular Oxygen. I. Oxidation of Terpinolene in Aqueous Dispersion[1]

BY J. N. BORGLIN, D. A. LISTER,[2] E. J. LORAND AND J. E. REESE

The autoxidation of terpenes has been the subject of numerous investigations, some of which date back almost a century; however, there have been no data available on the oxidation of terpinolene with molecular oxygen. This is surprising in view of the considerable interest in 1,4-diene systems (*e. g.*, linoleic acid) and the easy oxidizability of this terpene. The only oxidation studies published on terpinolene deal with the action of dilute potassium permanganate,[3] chromic acid,[4] and lead tetraacetate.[5] This neglect might have been due to the fact that terpinolene of satisfactory purity was not readily available. Recently this situation has changed, inasmuch as terpinolene of 85–90% purity can now be obtained by efficient fractionation of the higher boiling constituents of wood turpentine or of the monocyclic terpene by-products formed in the hydration of wood or gum turpentine. The main impurities remaining with terpinolene are 2,4(8)-*p*-menthadiene (isoterpinolene) and fenchone. By further fractionation in a high-efficiency column, the fenchone–terpinolene azeotrope can be eliminated to obtain a terpinolene of 95% or higher purity (b. p., 100 mm., 120.6°, d^{20}_{4} 0.8620, n^{20}_{D} 1.4900).

Oxidation of Terpinolene with Molecular Oxygen in a Single-phase System.—Since terpinolene has a methylene group (position 3 in Formula I) activated by two double bonds, oxidative attack should readily start here. Indeed, we have found at the outset that oxygen reacts with terpinolene more readily than with any of the other common terpenes, and that the oxidation does not require a catalyst, initiator, stronger than diffuse light. The reaction is not inhibited by the presence of other terpenes. At room temperature about one mole of oxygen per mole of terpinolene may thus be absorbed rather rapidly,



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(1) Presented before the Philadelphia Meeting of the American Chemical Society, April, 1950.

(2) Deceased.

(3) Wallach, *Ann.*, **362**, 292 (1908); **368**, 10 (1909).

(4) Henry and Paget, *J. Chem. Soc.*, **134**, 25 (1931).

(5) Ward, THIS JOURNAL, **60**, 325 (1938).

but further absorption is very slow. The reaction product is a light yellow, sirupy liquid of peroxidic character. It liberates iodine from potassium iodide solution to such an extent that the peroxide content calculated on a $C_{10}H_{16}O_2$ basis may be as high as, or higher than, 50%. Such high peroxide content may be obtained by initiating the oxidation at room temperature, then continuing at lower temperatures (0° or below). The product thus obtained is very unstable and decomposes rapidly even at room temperature, sometimes with explosive violence. Attempts to obtain simple products by chemical reduction or by catalytic hydrogenation were unsuccessful, as the reaction which ensued was decomposition (combined with partial polymerization) rather than reduction. The only substance that was identified was *p*-cymene, the remainder consisting of oxygen-bearing, polymerized substances. On the basis of molecular-weight determinations, these polymers appeared to be mainly dimers and trimers, the units containing hydroxyl, carbonyl, and epoxide groups. Part of the oxygen may be present in ether and acetal linkages.

More recent work has shed some light on the nature of the primary (peroxidic) oxidation product, the reactions involved in its formation and the changes in the double bond system, with special regard to prevailing ideas on the autoxidation of 1,4-diolefinic structures. This, however, will be the subject of a later paper in this series.

Oxidation of Terpinolene in Aqueous Dispersion.—The difficulties involved in the single-phase oxidation, in particular those encountered in the isolation of well-defined products, were overcome by a special oxidation technique. Some years ago it was observed[6] that, when terpinolene and water was agitated in the presence of air, the aqueous layer increased at the expense of the hydrocarbon. Evaporation of the water from the aqueous phase left a sirupy product part of which could be crystallized from solvents, such as ethanol–benzene or acetone. As will be seen later, the crystals consist of well-defined compounds (triols), while the sirupy crystallization residue is a mixture of related polyhydric compounds. A third group of oxidation products are found in the residual oil phase, a more or less viscous liquid containing water-immiscible oxygenated compounds.

Factors Influencing the Oxidation.—Temperature has a very pronounced effect not only on the rates of oxygen absorption, but also on the reaction products, *i. e.*, on the relative ratios of oils, water-solubles, and crystals. This is shown in Table I, which summarizes air-oxidation results obtained with a terpinolene:water ratio of 1:1 at various temperatures in the absence of catalysts. All experiments were run in the same equipment with the three phases intimately dispersed in one another.

TABLE I

EFFECT OF TEMPERATURE ON THE AIR-OXIDATION OF TERPINOLENE IN AQUEOUS DISPERSION

Oxidation temp., °C.	Reaction time, days	——Oxidation products, parts——		
		Oils[a]	H_2O-soluble[b]	Crystalline[a]
35	20	12	113	48
45	10	15	109	41
55	5	37	82	27
65	2.5	74	38	Nil

[a] Based on 100 parts (by weight) of terpinolene input.
[b] Includes both the crystalline and sirupy products.

The reaction is exothermic and about five times more rapid when oxygen is used instead of air. A still greater increase in the reaction rate can be effected by better dispersion of the air, or by the use of pressure.

When the usual oxidation catalysts, such as manganese, cobalt, and lead salts, oxides, etc., are used, the reaction is slowed down and much less water-soluble product is ultimately formed. Since the water-soluble product is probably the result of an intramolecular rearrangement of the hydroperoxide initially formed, it appears that the adverse effect of the catalysts is due to premature decomposition of the hydroperoxide. On the other hand, a small amount of acetic acid will nearly eliminate the induction period and 0.5–1.0% activated carbon will double the rate of reaction at 35–45°.

Oxidation Products

The **water-soluble product** is a light yellow, almost solid, sirupy liquid, which spontaneously crystallizes on standing for several days. On crystallization from ethyl acetate or alcohol–benzene (1:10), 15–20% of this product is recovered as menthenetriol, m. p. 136°. Crystallization from acetone, isopropyl acetate, nitromethane, or ether gives 40–45% recovery of a menthenetriol mixture. By fractional crystallization, this mixture can be separated into 3 components: (A) m. p. 136° (24%), (B) m. p. 121° (8–10%), and (C) m. p. 124° (8–10%). Component (C), m. p. 124°, is more soluble in acetone than the other two, which are very difficult to separate from each other. The crystallographic and optical data are shown in Table II[7] and the X-ray diffraction powder patterns in Fig. 1.[8]

Elementary analysis, hydroxyl content, molecular weight, and bromine number indicate that all three compounds have the empirical formula $C_{10}H_{18}O_3$; each contains one double bond and three hydroxyls, representing isomeric menthenetriols. They are volatile at low pressures, *e. g.*, the crystals melting at 136° can be distilled at 150–155° at 2.5 mm. Chemical behavior of the

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(6) Lister (to Hercules Powder Company) U. S. Patents 2,376,369 (May 22, 1945); 2,413,719 (Jan. 7, 1947); 2,413,720 (Jan. 7, 1947); 2,437,857 (Mar. 16, 1948).

(7) U. S. Patents 2,413,719 and 2,437,857; data obtained by W. A. O'Brien, Hercules Powder Company.

(8) Unpublished data, J. D. H. Donnay, Hercules Powder Company.

TABLE II

CRYSTALLOGRAPHIC AND OPTICAL PROPERTIES OF MENTHENETRIOLS

Isomer	A	B	C
Melting point, °C.	136	124	121
System	Monoclinic	Monoclinic	Triclinic
Refractive index	$\alpha = 0.510 \pm 0.003$	. . .	$\alpha = 1.54 \pm 0.01$
Optic angle 2V	49 ± 2°	*ca.* 90°	77 ± 3°
Dispersion	r > v	r > v	r > v
Sign of double refraction	(+)	(−)	(+)
Sign of elongation	. . .	. . .	(−)
Angle β	*ca.* 106°	94.5°	. . .
Optical orientation	Obtuse bisectrix = *b* axis	Optic normal β = *b* axis	. . .

triols will be discussed together with their structure in the second paper of this series.

These menthenetriols are undoubtedly the products of secondary reactions starting from the unstable hydroperoxide formed initially. It is likely that, first of all, an intramolecular oxidation or rearrangement, resulting in the conversion of the hydroperoxides to hydroxy epoxides, takes place. In the presence of water, the epoxide group is hydrolyzed to a glycol group, so that a menthenetriol is obtained. If an acid is present it also reacts with the epoxide to yield a monoester of the triol.[9]

The **sirupy product recovered from the crystallization mother liquors** still contains some 30–40% menthenetriols, the crystallization of which is hindered by the presence of other related compounds. (In one case, the sirupy product, after standing for four years at room temperature, did crystallize to yield more than 25% of a crystal mixture.) The other constituents are estimated as 15–18% monoacetates and monoformates of the triols, which result from the addition of acetic and formic acid to the intermediate hydroxy epoxide. Also present are 15–20% of dihydroxy ketones; these are probably formed in several steps and will be discussed in a later paper. Finally, menthenediols and their monoesters are also found to the extent of 30–34%. These diols and esters are also constituents of the oxidized oils, and their distribution between the two phases is such that the diol content of the oils is, in most cases, higher than that of the water-soluble residue.

Almost all of the crystalline triols are formed during the first half of the oxidation, *i. e.*, while the terpinolene concentration is relatively high. In one experiment, after the volume of the oil layer had dropped to half, the aqueous layer was replaced by water and the oxidation was continued. At the end of the reaction the second aqueous layer did not yield any crystals. While the main reaction of the hydroperoxide is rearrangement to the hydroxy epoxide and subsequent hydrolysis to the triols, the side reactions may consist in the isomerization of an epoxide to a ketone, or interaction between a hydroperoxide group (more likely its precursor, an $ROO\cdot$ free radical) and a double bond of another molecule, leading to an epoxide and by hydrolysis to a glycol.[9,10] These products remain principally in the oils and may be further oxidized directly by oxygen or by another molecule of hydroperoxide; the epoxy compounds formed may then be hydrolyzed by water or acids. These reactions become prominent in the later stages of the oxidation, when the terpinolene concentration is low. The resulting dihydroxy ketones and esters are water-soluble, and are, therefore, transferred to the aqueous layer.

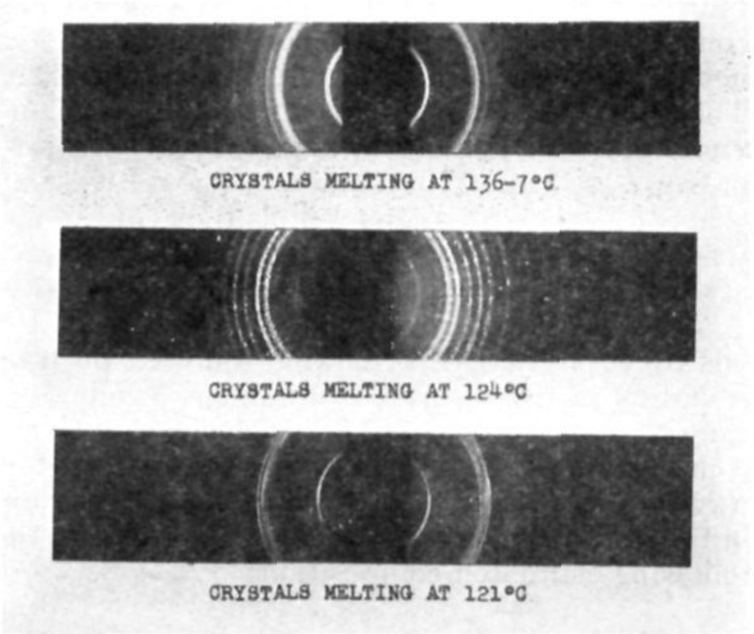

Fig. 1.—X-Ray diffraction powder patterns (Cu radiation) of menthenetriols.

The **oxidized oils** remaining at the end of the oxidation contain from below 1.0 to 2.0 atoms of oxygen per C_{10} unit, depending on the conditions and extent of oxidation. Their density, refractive index, and viscosity increase with increasing oxygen content. Analysis of these oils is difficult because of poor heat stability. The alcohols therein tend to dehydrate on distillation, even at reduced pressure. By an alkaline wash, however, the small amount of organic acids causing the dehydration can be removed so that the subsequent fractionation proceeds with hardly any dehydration. In this way, the oils can be separated into four main fractions: (a) hydrocarbons, (b) monohydric alcohols and ketones, (c) dihydric alcohols and their monoesters, and (d) a non-volatile polymerized residue. The relative size and composition of these fractions, and especially those of (a), depend on the extent of oxidation. The "light oils" (as obtained for instance in oxidations at 55° or higher) have a larger hydrocarbon fraction which, besides unreacted terpinolene, contains "isoterpinolene" (2,4(8)-*p*-menthadiene), fenchone, α-terpinene, and probably other minor impurities of terpinolene. The "heavy oils," which remain when high yields of water-solubles are ob-

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(9) Farmer and Sundralingam, *J. Chem. Soc.*, 121 (1942).

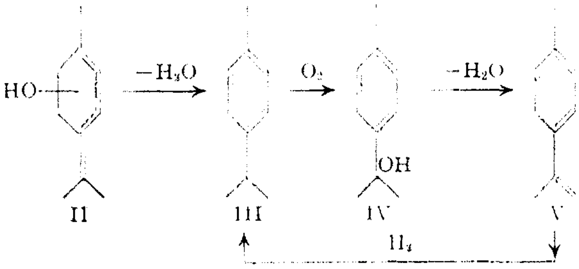
(10) Swift and Dollear, *J. Am. Oil Chem. Soc.*, **25**, 52 (1948).

tained (*i. e.*, the oxidation had been practically complete), have a smaller (a) fraction, which does not seem to contain any unreacted terpinolene. Their (c) and (d) fractions, on the other hand, are much larger. These two are separated by low-pressure (1–3 mm.) distillation. The dihydric alcohols of the distillate, as well as those in the water-soluble but non-crystallizing residue, are α,β-glycols, as shown by periodic acid titration.

More light was thrown on the composition of the oils by catalytic hydrogenation followed by fractionation of the saturated products. Analysis of the fractions made possible conclusions as to the composition of the original unstable oils. In this way, a heavy oil with practically no (a) fraction, but otherwise typical, appeared to possess the following estimated composition:

	%
Monohydric alcohols (diolefinic)	26
Dihydric alcohols	26
Monoesters (acetates or formates) of dihydric alcohols	4
Residue (average formula $C_{20}H_{30}O_4$)	44

The principal monohydric alcohol actually found by direct fractionation of the original oils is α,α-dimethyl-*p*-methylbenzyl alcohol (8-hydroxy-*p*-cymene) (IV), one of the main oxidation products of *p*-cymene (III), which, in turn, is probably formed by the dehydration of unstable menthadienols (II). In the course of hydrogenation, under the influence of heat and the acids present, the α,α-dimethyl-*p*-methylbenzyl alcohol also dehydrates and the α,p-dimethylstyrene (V) thus formed is then reduced to *p*-cymene.



Some work has been carried out on the oxidation of terpinolene in other dispersion media. In glacial acetic acid, the monoacetate of a triol which has been crystallized is the main product obtained. In alcohol, one of the products is a dihydric ether, while in aqueous ammonia a crystalline dihydric amine is also formed. These reactions and their products will be discussed in a later paper in this series.

Experimental

Air Oxidation of Terpinolene in the Presence of Water

Terpinolene.—A.S.T.M. boiling range (5–95%) 187.4–190.4°, $n^{20}D$ 1.4891, and $d^{15.6}$ 0.8639. Technical terpinolene (from by-product monocyclic terpenes) was steam-distilled over dilute sodium hydroxide and the distillate fractionated in a Fenske column of about 50-plate efficiency. The purity of the fraction selected for use in all the oxidation experiments was estimated (on the basis of further analytical fractionation, refractive index and reaction with maleic anhydride) as nearly 90%, the impurities being 2,4(8)-*p*-menthadiene, fenchone and α-terpinene.

Apparatus.—The oxidation apparatus consisted of a 1-liter, 3-necked flask equipped with a condenser, stirrer, thermometer, and air inlet tube terminating in a sintered glass disk (20-mm. diameter) opening directly beneath the stirrer. The reaction flask was held in a constant-temperature bath which could be regulated ±0.5°.

Procedure.—In a typical run, there was charged into this reactor 300 g. of terpinolene, 300 g. of distilled water, 1.5 g. of activated carbon, and 3 g. of acetic acid. The mixture was vigorously agitated, and air passed in at 6.75 liters per hour. The constant-temperature bath was held at 35°. The agitation was stopped each day, and the decrease of oil layer measured. After ten days the oil layer had almost disappeared and the oxidation was stopped.

Recovery.—The product was filtered and extracted twice with 100-ml. portions of benzene. Removal of the benzene under reduced pressure left a residue of 39 g. of a viscous yellow oil. The water was removed from the aqueous portion by distillation at reduced pressure, maintaining the temperature of the contents of the flask below 65°. There remained 339 g. of a light yellow thick sirup. The yield of water-soluble product was 83%, assuming the average molecular weight to be that of a *p*-menthenetriol.

Crystallization of Water-Soluble Product

From Ethyl Acetate.—The water-soluble product crystallizes on standing to form a solid mass of crystals embedded in a viscous fluid. Crystallization from three parts ethyl acetate gives 15–20% (based on water-soluble product) of small tabular crystals melting at 135–136° (all m. p. cor.). After repeated recrystallizations from ethyl acetate the melting point could be raised to 137°. These crystals appeared to be *p*-menthenetriol according to the analysis: *Anal.* Calcd. for $C_{10}H_{18}O_3$: C, 64.5; H, 9.68. Found: C, 64.4; H, 9.61.

	Calcd., %	Found, %
Bromine no. ($KBr-KBrO_3$)	86	102
OH (Zerewitinoff)	27.4	27.1
OH (Acetylation)	(9.1 for 1 OH)	10.9
Molecular weight (Rast)	186	192

The low acetylation value indicates that the product has two tertiary hydroxyl groups and one secondary.

A similar yield of crystals melting at 135–136° was obtained by dissolving the water-soluble product in one part anhydrous alcohol and adding ten parts benzene.

From Acetone, Ether, Isopropyl Acetate or Nitromethane.—Crystallization of the water-soluble product from two parts of acetone gave 40% crystals; from three parts of ether, 40% (by merely triturating the crude crystal mass with ether); from two parts of isopropyl acetate, 45%; and from two parts of nitromethane, 45% (by trituration of the crude crystal mass). These crystalline products have indefinite melting points, usually in the range of 103–117°, and appear to be a mixture of isomeric *p*-menthenetriols.

Fractional Crystallization.—One thousand grams of water-soluble product was refluxed with 2000 ml. of ethyl acetate, cooled, and the short tabular crystals filtered off: Fraction I, 164 g., m. p. 135–136°. The ethyl acetate was removed from the mother liquor under reduced pressure, 1500 ml. of acetone added, refluxed, cooled, and crystals filtered off; Fraction II, 155 g., m. p. 105–110°. A 1000-ml. portion of acetone was distilled from the mother liquor, 1500 ml. of benzene added, and the mixture allowed to stand at 0–3° for several weeks. Crystals were formed slowly; Fraction III, 134 g., m. p. 95–112°. Final mother liquor, after removal of the solvents, amounted to 533 g. of thick sirup. Systematic fractional crystallization from acetone starting with Fractions II and III after three steps gave separation into large prismatic crystals; Fraction V, 80 g., m. p. 124–125°, which was more soluble in acetone and Fraction IV, 160 g., m. p. 105–110°, which was less soluble in acetone. Fraction IV was systematically crystallized from 1:1 ethyl acetate–acetone mixture, and after six steps no separation was effected. One fraction, however, happened to crystallize in large elongated tabular crystals which were removed by hand with tweezers, obtaining in this manner Fraction VI, 2.0 g., m. p. 121–122°. X-Ray diffraction indicated that Fraction IV was a 50:50 mixture of the crystals of m. p. 135–136° and 121–122°. Fraction IV could be separated into its two components by careful fractional crystallization from acetone. Analyses indicated that the two new crystal forms were also isomeric *p*-menthenetriols:

		Calcd. for $C_{10}H_{18}O_3$	Crystals of m. p., 124–125°	Crystals of m. p., 121–122°
Anal., %	Carbon	64.5	64.7	64.7
	Hydrogen	9.68	9.77	9.90
Bromine no., $KBr-KBrO_3$		86	56	82

The approximate composition of the water-soluble product in this instance was estimated as 24.4% *p*-menthenetriol, m. p. 135–6°, 8.0% *p*-menthenetriol, m. p. 124–5°, 8.0% *p*-menthenetriol, m. p. 121–122°, and 53.3% noncrystalline residue. Experimental losses during fractional crystallizations were 6.3%. In subsequent work slightly higher yields were estimated for the two lower melting crystal species, and the correct melting points, after repeated crystallization of the three isomers, were 136°, 124°, and 121°.

Composition of the Non-crystalline Residue.—Analysis of this residue gave:

Acid no.	10
Saponification no.	50
Bromine no. ($KBr-KBrO_3$)	52
Carbonyl (Bryant-Smith), %	2.8
OH (Zerewitinoff), %	21.5
Carbon, %	65.8
Hydrogen, %	9.50
C_{10} (average formula)	$C_{10}H_{17.3}O_{2.8}$

The saponification number indicates 16.4% monoacetate of a *p*-menthenetriol, and the carbonyl value indicates 18.5% of a dihydroxy ketone or similar compound. The bromine number shows that most of the compounds still contain a double bond. The low oxygen content of the average formula is probably due to menthenediols.

A 387-g. portion of non-crystalline residue was distilled at reduced pressure. After a distillate of 123 g. passed over between 82° (0.5 mm.) and 112° (2.0 mm.), decomposition and dehydration started and the distillation had to be stopped. The distillate appeared to be mainly *p*-menthadienols, perhaps formed by the dehydration of a triol.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.4; H, 9.53. Found: C, 71.5; H, 9.25. Therefore, 31.8% *p*-menthadienols was present in the non-crystalline residue. The remainder of 33.5% is probably made up of *p*-menthenetriols which are very difficult to crystallize because of the interference of the other components. (A sample of such sirupy residue did crystallize on standing for several years.) The non-crystalline residue was saponified, acidified, and the acids thus liberated found to be one-third formic and two-thirds acetic acid by the method of Richmond.[11]

Fractionation of Oxidized oils

(a) Lightly Oxidized Oil Containing an Average of 1 Atom Oxygen per Molecule.—This type oil is obtained when low yields of water-soluble product are formed, because of higher temperature, say 55°, or premature termination of the oxidation. The oil has a density lower than water and floats over the aqueous layer. In one group of experiments, 5300 g. of terpinolene was oxidized in 18 portions, each in the presence of an amount of water equal to the amount of terpinolene used, at temperatures ranging from 35 to 55°. Yields obtained were 4525 g. of water-soluble product and 1687 g. of oil which on steam distillation gave 1128 g. of distillate and 397 g. of residue.

The distillate was fractionated in a 40-plate Fenske column at 50 mm. pressure into 37 small cuts which were combined into 6 large cuts

Cut	B. p., °C.	$n^{20}D$	Weight, g.
1	79–91	1.4729	46.2
2	91–92	1.4779–1.4812	109.2
3	92–98	1.4811–1.4848	183.3
4	98–101	1.4860–1.4993	368.3
5	101–112	1.5032–1.5091–1.4920	75.4
6	112–131	1.4785–1.5112	98.9
Residue	.....	1.5214	184.6
			1065.9

Cut 2 gave a strongly positive maleic anhydride test for conjugation and was probably mainly α-terpinene. The high bromine number ($KBr—KBrO_3$ 194) of cut 5, together with the boiling point and refractive index, indicates that this cut contains, besides unchanged terpinolene, either much 2,4(8)-*p*-menthadiene or also some hydrocarbons of high refractive index. Since dehydration began at the start of cut 4, it is very probably that α,α-dimethyl *p*-methylbenzyl alcohol was dehydrated to form α,*p*-dimethylstyrene ($n^{20}D$ 1.5357). Cut 6 appeared to be a mixture of terpene ketones and alcohols. Dehydration became so excessive that the fractionation had to be stopped.

The steam distillation residue was distilled giving 108.4 g. of dihydric alcohol cut (b. p. 79° (2.5 mm.)–107° (1.3 mm.) and $n^{20}D$ 1.5110) and 262.5 g. of polymeric residue.

ESTIMATED COMPOSITION OF LIGHTLY OXIDIZED OIL

47%	terpenes (probably terpinolene, α-terpinene, 2,4(8)-*p*-menthadiene, and other terpenes), and also some α,*p*-dimethylstyrene (from dehydration of α,α-dimethyl-*p*-methylbenzyl alcohol)
17%	monohydric alcohols and ketones (including some α,α-dimethyl-*p*-methylbenzyl alcohol)
6%	dihydric alcohols
15%	polymer
15%	loss

(b) Highly Oxidized Oil Containing an Average of 2 Atoms Oxygen per Molecule.—This type oil is obtained when high yields of water-soluble product are formed, *e. g.*, at temperatures below 45°. The oil is viscous, has a higher density than water, and frequently sinks below the aqueous layer. Such an oil was obtained when 2000 g. of terpinolene, in six portions, was oxidized in the presence of a total of 3200 g. of water and 12 g. of acetic acid at 40°. A total of 2219 g. of water-soluble product and 198 g. of heavy oil was recovered.

The oil cannot be distilled if traces of acid are present because excessive dehydration will occur. After an alkaline wash, however, a 162-g. portion of oil was successfully fractionated in a 20-plate Fenske column at 24 mm. pressure:

Cut	B. p, °C.	$n^{20}D$	Weight, g.
1	72–84	1.4800	22.7
2	84–116	1.4877	14.3
3	116	1.5160	22.8
Residue	.....	....	79.3
Holdup and loss	.....	....	22.9
			162.0

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[11] Richmond, *Analyst*, **20**, 193, 217 (1895).

Cuts 1 and 2 appeared to be mainly terpinolene (b. p. 84° (24 mm.) and $n^{20}D$ 1.4888) with some lower boiling terpenes. Cut 3 was identified as mainly α,α-dimethyl-*p*-methylbenzyl alcohol (b. p. 118° (24 mm.) and $n^{20}D$ 1.5185) by the phenylurethan m. p. 119–20° (lit. 118–119°).

The highly oxidized oil also is made stable by hydrogenation prior to distillation. A 461-g. portion of oil was smoothly hydrogenated with 50 g. of Raney nickel catalyst at temperatures from 90–132°, 9.2 g. of hydrogen being absorbed. The recovered oil, 470 g., was steam-distilled giving 121 g. of distillate and 349 g. of residue. The distillate was fractionated into 93 g. of *p*-cymene (b. p. 76–77° (26 mm.), $n^{20}D$ 1.4878–1.4902) and a residue of 27 g. of monohydric alcohol. The steam distillation residue was distilled giving 104 g. of dihydric alcohol (b. p. 110° (0.2 mm.)–120° (0.05 mm.)) and leaving 188 g. of solid polymeric residue.

Dihydric Alcohol Cut.—*Anal.* Calcd. for $C_{10}H_{20}O_2$: C, 69.8; H, 11.62. *Anal.* Calcd. for $C_{10}H_{18}O_2$: C, 70.6; H, 10.6. Found: C, 70.4; H, 10.91; saponification no., 40. This indicates 15% monoacetate of the dihydric alcohol.

Polymeric Residue.—Found: C, 72.6; H, 9.17; mol. wt. (Rast), 346 ($C_{20}H_{30.3}O_{3.4}$).

ESTIMATED COMPOSITION OF HYDROGENATED OXIDIZED OIL

20.2%	*p*-cymene
5.8	monohydric alcohol
22.7	dihydric alcohol
40.8	polymer
10.5	loss

Summary

1. The primary product of terpinolene oxidation with molecular oxygen in a single liquid phase is a very unstable, iodine-liberating peroxidic substance which cannot be reduced or decomposed to related simple compounds.

2. In the presence of an aqueous phase, large amounts (as high as 120 parts per 100 parts terpinolene) of water-soluble products can be obtained. The major constituents (about 40–45% can be recovered) are three crystalline menthenetriols melting at 136°, 124° and 121°, respectively.

3. The estimated composition of the non-crystallizing portion of the water-soluble products in a typical case was about 16% monoesters (formates and acetates) of menthenetriols, 18% dihydroxy ketones, 32% menthenediols, and an additional 34% menthenetriols.

4. As by-products, water-immiscible "oxidized oils," apparently containing menthadienols, menthenediols, and their esters, ketones, and oxygen-containing dimers, are also recovered in varying amounts.

WILMINGTON, DELAWARE RECEIVED DECEMBER 9, 1949

[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

Oxidation of Terpenes with Molecular Oxygen. II. Oxidation Products of Terpinolene[1]

BY E. J. LORAND AND J. E. REESE

As shown in the first paper in this series,[2] when terpinolene is oxidized with molecular oxygen in the presence of an aqueous phase, the major part of the reaction products appears in the aqueous layer. About 40% of the water-soluble material was recovered in crystalline form, the crystals having three distinct forms melting at 136° (I), 124° (II), and 121° (III), respectively. Elementary analysis, hydroxyl contents, molecular weights, catalytic hydrogen absorption, and bromine numbers indicated that all three are menthenetriols. Further confirmation of this point was offered by conversion of the mixture of crude crystals to the triacetate stage by acetylation with acetic anhydride-pyridine. It remained to determine the chemical properties of these crystalline compounds and the non-crystalline portion (IV), as well as the structures of the crystalline isomers and, in particular, the positions of the hydroxyls and of the double bond.

While a number of saturated triols of the *p*-menthane series are known, only one unsaturated triol has been described[3] which was assigned the structure of 1-*p*-menthene-4,6,7-triol, although this was not proved. According to Wallach's formula, it has no α,β-glycol group, while our crystalline isomers, as will be seen, all have one pair of hydroxyls on neighboring carbon atoms. They must, therefore, be considered new compounds. This also appears to be the case with the constituents of IV, which, as will be recalled, contained besides the triols their monoesters (acetates and formates) and dihydroxy ketones.

As it was evident from the outset that in all these compounds there must be present one or more tertiary hydroxyls, numerous dehydration experiments were carried out. It was found that the ease of dehydration decreased in the following sequence: the non-crystalline water-solubles (IV), the total (crystalline + non-crystalline) water-solubles (V), the total crystalline products or "mixed crystals" (VI), and the crystals melting point 136° (I). The dehydration methods applied included heating with water under pressure, with and without simultaneous catalytic hydrogenation, treatment with dilute aqueous acids of both the original triols and their hydrogenation products, and hydrogenation at room temperature in the presence of concentrated phosphoric acid. The dehydration products included, depending on

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[1] Presented before the Philadelphia Meeting of the American Chemical Society, April, 1950.

[2] Borglin, Lister, Lorand and Reese, THIS JOURNAL, **72**, 4591 (1950).

[3] Wallach, *Ann.*, **360**, 96 (1908).