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 ($C_{20}H_{30.5}O_{3.4}$).

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).

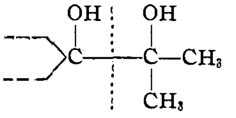
[3] Wallach, *Ann.*, **360**, 96 (1908).

conditions, hydrocarbons (*p*-menthane, *p*-cymene, α,p-dimethylstyrene), unsaturated and saturated alcohols (*e. g.*, carvomenthol), ketones, and dihydric alcohols. The differences in behavior indicated that structural differences must exist not only between the crystalline bodies and the noncrystalline portion, but also between the different crystalline isomers. The isomer I was hydrogenated with Raney nickel as catalyst to obtain a product which crystallized as a hemihydrate (VII) and had a melting point of 81° in contrast to Wallach's 1,2,8-menthanetriol[4] obtained by the permanganate oxidation of α-terpineol, which is anhydrous and melts at 122°. By drying in vacuum, the half mole of water of crystallization can be removed from our product, and the anhydrous crystals melt at 102°. Baeyer's 1,4,8-*p*-menthanetriol[5] crystallizes as a monohydrate melting at 95–96°, while the anhydrous compound melts at 110–112°. None of the other known menthanetriols melts at 81 or 102°; this, however, may be due to *cis–trans* isomerism; *e. g.*, in Wallach's triol, the 1,2-glycol is *cis*, while our triol might have a *trans*-glycol group because of its formation from an epoxide by hydration.

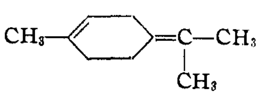
The menthanetriol hemihydrate (VII) could be completely esterified with both acetic and propionic anhydride in pyridine. The resulting triesters are distillable at 0.1 mm. pressure in the ranges of 108–111° and 122–125°, respectively. In a similar way the parent menthenetriol (I) yielded esters approximating the trisubstituted stage.

The menthanetriol hemihydrate (VII) was quite resistant to dehydration. With iodine in boiling cymene, only the water of crystallization was eliminated. A similar result was obtained with a combination of phthalic anhydride and silica gel. It required dilute sulfuric acid (10%) to give a steam-volatile oil, consisting mainly of *p*-cymene (35%) and apparently unsaturated ketones (52%). This, together with previous dehydration experiments, leads to the conclusion that isomer I has at least one secondary hydroxyl and at least one tertiary hydroxyl. It is also probable that one tertiary and one secondary hydroxyl are on adjacent carbon atoms. That IV, V and VI also give varying amounts of ketones by a suitable dehydration process may be due to the presence of I, or another isomer having a secondary hydroxyl, or both.

A more definite indication of the relative position of the hydroxyls was obtained by periodic acid titration, which showed the presence of one α,β-glycol group not only in each of the three isomeric triols, but also in IV. On the other hand, only one of the isomers (II) yielded acetone when oxidized with periodic acid. This indicates the presence of hydroxyls in positions 4 and 8 of the terpinolene molecule, *i. e.*, a substituted pinacol (A), as



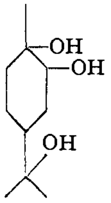
A



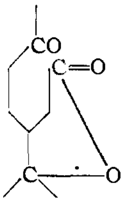
B

if derived from the esocyclic double bond of terpinolene (B). The other two isomers (I and III) must have hydroxyls on two other adjacent carbons, such as 1 and 2, *i. e.*, in place of the cyclic double bond of the terpinolene skeleton. Ozonolysis of I gave similar results, as no acetone could be detected. An attempt was made to isolate the periodic acid oxidation product of I by preparing its 2,4-dinitrophenylhydrazone, but no crystalline compound was obtained. The same was the case with III. The periodic acid oxidation of VII, as was expected from the behavior of the parent menthenetriol (I), did not produce acetone.

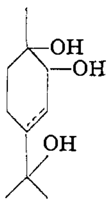
Wallach[6,7,8] showed that his *dl*-1,2,8-menthanetriol (C) (m. p. 121°), as obtained from α-terpineol by permanganate oxidation, can be oxidized with chromic acid to the ketolactone (D) (homoterpenyl methyl ketone) melting point 64°.



C



D



E

Our menthanetriol VII was successfully oxidized to the same ketolactone (melting point, semicarbazone and oxime); therefore, it must have the same carbon skeleton and the hydroxyls on the same carbons (1, 2 and 8) as Wallach's. This leaves the position of the double bond in I as the only uncertainty. It was thought that hydroxylation of the double bond, *e. g.*, by permanganate oxidation, would yield a pentahydric alcohol, periodic acid titration of which might show the position of the double bond; *e. g.*, five adjacent hydroxyls would indicate a double bond position as in (E). Unfortunately, the permanganate oxidation of both I and II was unsuccessful, as most of the material used was recovered unchanged.

More success was attained with peracetic acid, although it was very difficult to obtain a crystalline product. The product obtained was not the pentahydric alcohol expected, but rather a trihydric cineole, possibly one of the following three structures, where the broken line indicates the potential position of the double bond of the triol. Of these structures, H appears to be least probable.

Periodic acid titration of the trihydric cineole

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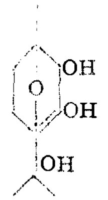
[4] Wallach, *Ann.*, **275**, 151 (1893).

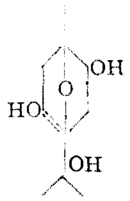
[5] A. Baeyer, *Ber.*, **28**, 2296 (1895).

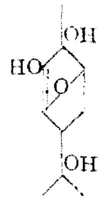
[6] Wallach, *Ann.*, **277**, 110 (1893).

[7] Wallach, *Ber.*, **28**, 1775 (1895).

[8] Tiemann and Semmler, *ibid.*, **28**, 1778 (1895).

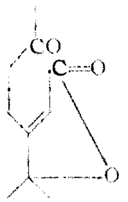

F

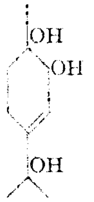

G


H

shows that the first mole of periodate is consumed relatively rapidly; then, at a decreasing rate, three more moles are used up. It appears, therefore, that one α,β-glycol group is actually present, while three more are formed by the gradual hydrolysis of the ether in the strongly acid medium. In this way, the final periodic acid consumption indicates approximately 5 adjacent hydroxyls, which is consistent with structure F and with the conclusion that the double bond is located between carbons 3 and 4.

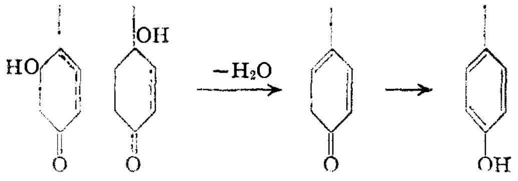
In order to strengthen this conclusion, an attempt was made to oxidize I with chromic acid. Henry and Paget[9] showed that in the chromic acid oxidation of terpinolene the main constituent of the non-acidic fraction obtained is β-thujaketolactone (semicarbazone m. p. 222–223°), which has a 3,4-double bond (J). Following largely Wallach's procedure[6] in the oxidation of I, the neutral fraction of the reaction product gave the same semicarbazone.


J


K

It is, therefore, evident that the position of the double bond in I is the same as in β-thujaketolactone (*i. e.*, 3,4) so that the structure of I must be that represented by K, *i. e.*, it must be a 3-*p*-menthene-1,2,8-triol. The *trans* configuration must be assigned to hydroxyls 1 and 2, because the hydrogenation product (VII) is different from Wallach's menthanetriol, which is *cis*. This is in harmony with the assumption that I must have been formed by the hydration of the 1,2-epoxide.

Isomer II, as stated before, yields acetone on periodic acid oxidation; it must, therefore, have hydroxyls in 4 and 8 positions. This leaves only the position of the third hydroxyl and that of the double bond undetermined. As the major oxidation product must be an unsaturated keto alcohol, the hydroxyl group may be either in 1 or 6 position, which limits the double bond to 2,3 and 1,2. Formula L represents two alternative forms with the hydroxyl in 6 position, while Formula M stands for the only form possible with the hydroxyl in position 1.

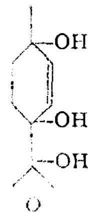

L M N

Assuming that structure M is correct, dehydration should lead to *p*-cresol.

In one experiment, the oxidation with pure periodic acid produced a compound which had a very strong ultraviolet absorption band at 226 mμ, indicating a double bond conjugated to a ketone carbonyl group. It was soluble in sodium hydroxide, but insoluble in sodium carbonate. Mineral acid at room temperature did not convert it to a phenol; however, heating with dilute sulfuric acid in a water-bath produced *p*-cresol which was identified by ultraviolet absorption. The intermediate compound was not identified, but its ultraviolet absorption is not inconsistent with structure M.

Another approach to structural proof was based on the similarity of A. Baeyer's[5] 1,4,8-*p*-menthanetriol to II, which also has hydroxyls in positions 4 and 8. Hydrogen bromide converts this triol to the corresponding tribromide which is identical with Wallach's tribromide,[10] as obtained from dipentene by the addition of 2 moles of hydrogen bromide, followed by bromination in position 4. If the position of the third hydroxyl in II is the same as in Baeyer's menthanetriol, hydrogenation of the former followed by reaction with hydrogen bromide in acetic acid should yield Wallach's tribromide, melting point 110°.

Hydrogenation of II in aqueous solution with PtO_2 catalyst gave a sirupy product which was crystallized from ethyl acetate (VIII); melting point 139–140°, as against Bayer's 1,4,8-*p*-menthanetriol of melting point 110–112°. The two saturated triols evidently were not identical, but still could be stereoisomers, in which case they would yield the same tribromide. In fact, the tribromide prepared from VIII proved identical with Wallach's, *i. e.*, it gave a satisfactory mixed melting point with an authentic 1,4,8-tribromo-*p*-menthane. In view of the positions of the hydroxyl thus determined, it is obvious that in the original menthenetriol (II) the double bond, as shown in structure (O), can have only one position, that in 2,3.


O

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[9] Henry and Paget, *J. Chem. Soc.*, **134**, 25-31 (1931).

[10] Wallach, *Ann.*, **264**, 25 (1891).

This, of course, is in agreement with the conclusions drawn from the dehydration-rearrangement of the periodic acid oxidation product, as shown above. It can be, therefore, concluded that II is a 2-*p*-menthene-1,4,8-triol.

The structure determination of I and II should throw some light on the mechanism of their formation, and, in general, on the oxidation process in aqueous dispersion. There is no doubt that the primary product of oxidation is a peroxidic substance which liberates iodine from hydriodic acid solution. Although the reaction conditions (higher than room temperature and the presence of water) do not seem to favor the accumulation of this peroxidic product, the presence of a few per cent. has been found repeatedly. According to the prevailing ideas, the most likely place of attack by oxygen is the 3 carbon atom which is flanked by a double bond on each side. The autoxidation of a similar methylene-interrupted double-bond system, such as occurs in ethyl linolenate, was investigated by Farmer.[11] His interpretation of the conjugative changes appears to be applicable to the case of terpinolene which possesses a pentadiene system similar to that considered by Farmer. The oxidative attack on the methylene group activated by

$$R'\text{—}\underline{CH}\text{=}CH\text{—}\underset{*}{CH}\text{—}CH\text{=}\underline{CH}\text{—}R''$$

both double bonds starts with the loss of a hydrogen, which leaves a diolefinic-free radical. Resonance stabilization should produce the following two forms

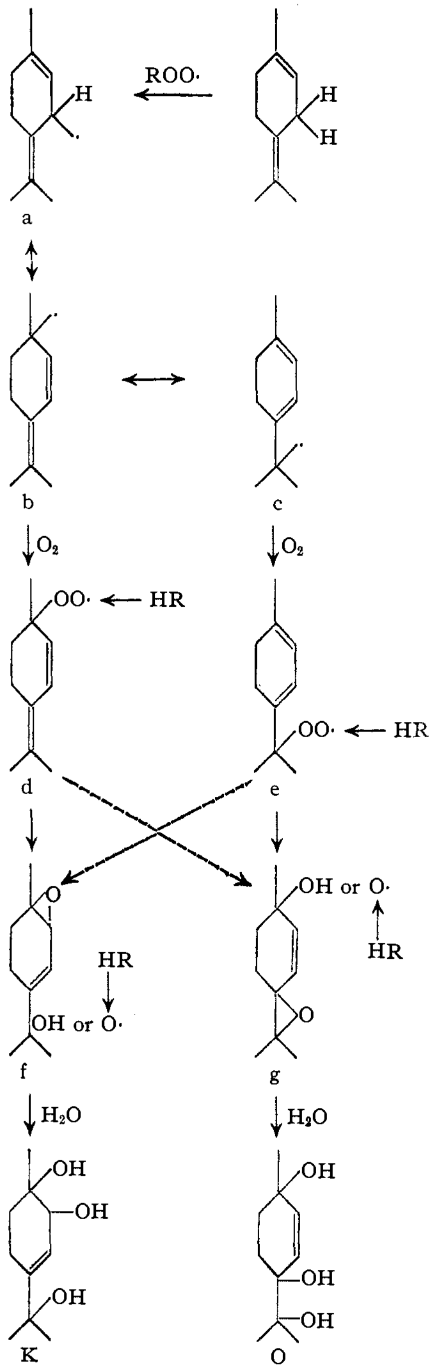
$$R'\text{—}\underset{*}{CH}\text{—}CH\text{=}CH\text{—}CH\text{=}CH\text{—}R'' \text{ and }$$
$$R'\text{—}CH\text{=}CH\text{—}CH\text{=}CH\text{—}\underset{*}{CH}\text{—}R''$$

Addition first of an oxygen molecule and then a hydrogen atom ensues on the radical centers, resulting in two conjugated diene hydroperoxides.

Independently of Farmer, C. C. Price[12] suggested a similar reaction mechanism for the oxidative formation of our menthenetriols, as shown by the sequence below.

The free radicals b and c may take up an oxygen molecule to form the peroxy free radicals d and e. These, in turn, may extract a hydrogen from a hydrocarbon molecule, and the resulting hydroperoxides may rearrange by the 1,4 addition of the hydroperoxyl group to the conjugated double bond system, as indicated by the solid arrows, leading to f and g. On the other hand, the intramolecular oxidation in the free radicals d and e, as indicated by the broken arrows, cannot be ruled out. This reaction would be somewhat analogous to the action of peracids. The resulting free radicals f and g would then extract a hydrogen from a hydrocarbon molecule. Hydrolysis of the hydroxy epoxides thus formed leads to structures K and O or Crystals I and II.

This leaves the structure and formation of isomer III undecided. Work is in progress on this problem.



Experimental

Acetylation of the Crystalline Menthenetriol Mixture (VI).—One mole of "mixed crystals" prepared by air oxidation of terpinolene[2] was dissolved in 7 moles of pyridine and 6 moles of acetic anhydride was added gradually to the solution with vigorous shaking and occasional cooling. The mixture was then heated for 7 days in a constant-temperature bath at 55°. After dilution with benzene, the solution was washed free of pyridine, etc., with H_2O and 1% HCl. By distillation at 0.25-mm. pressure.

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[11] Farmer, Sutton and Koch, *J. Chem. Soc.*, 541 (1943).

[12] Verbal communication in the fall of 1943.

a cut (172 g.) distilling at 125° was obtained. Its saponification number (539.5) indicates a triacetate (theory 541.6).

The triacetate and tripropionate of the menthanetriol obtained from I by hydrogenation were prepared similarly (time of acetylation, 13 days, temperature 85°). Triacetate boiling point 108–111° at 0.1 mm. and tripropionate boiling point 122–125° at 0.1 mm.

Hydrogenation of *p*-Menthenetriol, Melting Point 136°.—A solution of 322 g. of I in 700 cc. of water was smoothly hydrogenated in a rocker-type autoclave, using 75 g. of Raney nickel at 3000 lb./sq. in. initial pressure and a temperature of 120–140° in 2.5 hours. The estimated hydrogen absorption was 3.82 g. (theory, 3.46 g.). The product was extracted with benzene to remove about 1 g. of oily product, and after distilling off the water at reduced pressure, 331 g. of colorless water-soluble sirup was recovered. A 25.8-g. portion of this sirup was crystallized from ethyl acetate, giving 11.6 g. of crystals, melting point 81° (VII). Elementary analysis indicates that the menthanetriol is a hemihydrate.

Anal. Calcd. for $C_{10}H_{20}O_3 \cdot {}^1/_2H_2O$: C, 61.00; H, 10.68. Found: C, 61.57; H, 10.78.

A small sample of the hemihydrate was dried in a vacuum oven at 65° for 23 hours, melting point 102°.

Anal. Calcd. for $C_{10}H_{20}O_3$: C, 63.8; H, 10.64. Found: C, 64.0; H, 10.68.

Dehydration of *p*-Menthanetriol (VII) with Dilute Sulfuric Acid.—A solution of 129 g. of hydrogenated 1 in 400 g. of 10% H_2SO_4 was steam-distilled immediately. The oily product thus obtained was fractionated in a 20-plate packed column. The fractions contained about 30 g. of *p*-cymene (b. p. at 25 mm. 76°, $n^{20}D$ 1.4905) and 44 g. of apparently unsaturated ketones[13] ($n^{20}D$ 1.4800–1.4820; bromine number 110).

Periodic Acid Titration of the *p*-Menthenetriols.—The method of Fleury and Fatome[14] was applied to the three isomers and to the non-crystalline portion (IV).

Compound	M. p., °C.	Moles α,β-glycol found
I	136	0.96
II	124	1.04
III	121	0.87
IV	. . .	0.91

Periodic Acid Oxidation of the Menthenetriols.—(1) A solution of 2.45 g. of potassium metaperiodate in 960 cc. of water and 40 cc. of 25% sulfuric acid was added to 1.98 g. of I. After standing fifteen minutes at room temperature, the solution was neutralized and about half of it distilled. The distillate gave a negative test for acetone by Snell's vanillin method.[15] The residue gave a dark precipitate with 2,4-dinitrophenylhydrazine, melting point 100–125°. No crystallinity could be detected under the microscope. In another oxidation experiment, the undistilled solution gave a yellow-orange precipitate with 2,4-dinitrophenylhydrazine, which, however, turned black after standing for a day.

(2) A repetition of the above procedure with III led to a negative test for acetone in the distillate and, from the residue, a nearly black non-crystalline precipitate with 2,4-dinitrophenylhydrazine, melting point 100–135°.

(3) Under similar conditions, II gave a positive test for acetone, indicating the presence of 0.4 g. in the distillate (theory 0.62 g.). The distillate also gave a yellow 2,4-dinitrophenylhydrazone, melting point 125° (acetone gives a compound of melting point 128°). The residue gave a brown precipitate with 2,4-dinitrophenylhydrazine, melting point 176–177°.

Peracetic Acid Oxidation of *p*-Menthenetriol (I).—Peracetic acid solution, 300 cc., containing 1.0 mole active oxygen (prepared by heating AcOH and hydrogen peroxide with 1% sulfuric acid catalyst at 50° for one hour) was added dropwise to 93 g. of I (0.5 mole) at 25–30° over several hours. The catalyst was neutralized with barium acetate, the acetic acid distilled off *in vacuo* at near room temperature, the residue dissolved in excess water, and the barium sulfate filtered off. Removal of the water *in vacuo* gave 70.8 g. of brown, almost solid sirup.

Analyses	Calcd. for $C_{10}H_{18}O_4$	Found
Acid number	0	0.45
Saponification number	0	29.0
OH (Zere.)	25.2	24.7

Anal. Calcd. for $C_{10}H_{18}O_4 \cdot {}^1/_2H_2O$: C, 56.8; H, 9.0. Found: C, 56.33; H, 8.96.

After numerous attempts, the product was brought to partial crystallization from a mixture of ether and ethyl acetate. White needles, melting point 117–118°, were obtained in 4% yield, which was gradually increased by further crops.

Anal. Calcd. for $C_{10}H_{18}O_4$: C, 59.42; H, 8.92. Found: C, 59.26; H, 8.89.

Periodic Acid Titration of the Trihydric Cineole.—Fleury's method[14] was applied using 5 cc. 0.1 *M* free periodic acid solution for 10–15-mg. samples of the cineole.

Time of oxidation	15 min.	30 min.	60 min.	2 hr.	4 hr.	6 hr.	16 hr.	44 hr.
Mole HIO_4 consumed	0.3	0.5	0.7	1.0	1.3	1.6	2.2	3.8

Chromic Acid Oxidation of the *p*-Menthanetriol VII.—A solution of 23 g. of VII in 14 cc. of water was oxidized with 16 g. of CrO_3 in 40 cc. of 35% sulfuric acid by Wallach's method.[6] A total of 12.6 g. of pale yellow crystals, melting point 60–61°, was obtained. After recrystallization from water, these melted at 62–63°, and no melting point depression was observed when the crystals were mixed with authentic homoterpenyl methyl ketone prepared from α-terpineol by oxidation first with $KMnO_4$, then with Beckman acid. The ketolactone gave a yellow 2,4-dinitrophenylhydrazone, melting point 160°. The semicarbazone melts at 209–210°, which compares with melting point 210.5–211° of the semicarbazone prepared from an authentic homoterpenyl methyl ketone (obtained from α-terpineol by Wallach's method). The mixed melting point was 209–209.5°. It is peculiar that Wallach[16] gave 199–200° as the melting point for his derivative, while Simonsen[17] reports 206–207°.

Chromic Acid Oxidation of the *p*-Menthenetriol I.—To 23.25 g. of I in 34 cc. of water, a solution of 16 g. of chromic anhydride in 40 cc. of 35% sulfuric acid was added in small portions while cooling with tap water. In about fifteen minutes the reaction was finished. The reaction mixture was extracted several times with chloroform, the solvent distilled off, and the residue redissolved in chloroform–ether. This solution was extracted repeatedly with dilute sodium carbonate, then the solvents distilled off. The neutral, viscous residue weighed 5.1 g. and gave a semicarbazone melting at 222–223° (the same as that of "β-thujaketolactone" of Henry and Paget.[9]

Conversion of *p*-Menthenetriol II to *p*-Cresol.—A solution of 2.5 g. of crystalline periodic acid (H_5IO_6) in 50 ml. of water was mixed with a solution of 1.86 g. (0.01 mole) of II in 30 ml. of water. After thirty minutes practically all of the periodic acid was consumed; nevertheless, the mixture was allowed to stand for another hour before extraction five times with ether. The extract was shaken out with dilute sodium hydroxide which removed all the solute, as the ether evaporated without residue. After acidification, the solution was extracted three times with copious amounts of ether. Evaporation of the ether left an amber liquid residue of 0.15 g. One drop of the residue was

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[13] Bryant and Smith, THIS JOURNAL, **57**, 57 (1937).

[14] Fleury and Fatome, *J. pharm. chim.*, **21**, 247 (1935).

[15] Snell, "Colorimetric Methods of Analysis," Vol. II, D. Van Nostrand Co., New York, N. Y., 1937, p. 96.

[16] Wallach, *Ann.*, **291**, 343 (1896).

[17] Owen and Simonsen, *J. Chem. Soc.*, **135**, 1428 (1932).

heated in a test-tube with 5–6 drops of 0.5 H_2SO_4 for 10–15 minutes in a steam-bath. A strong cresolic odor was noticed. In a larger sample similarly treated *p*-cresol was identified and determined by ultraviolet analysis (absorption band at 279 mμ), which also showed a strong absorption band at 226 mμ in the acidified and ether-extracted alkaline wash. An even stronger band at the same wave length was obtained with the original (although ether-extracted) reaction mixture. The location of the band is consistent with the assumption of structure M.

Hydrogenation of *p*-Menthenetriol II.—1.69 g. of II was dissolved in 40 ml. water and hydrogenated at atmospheric pressure in a closed system which allowed the volumetric measurement of the hydrogen absorbed; 1.2 g. of platinum oxide catalyst was used and the mixture was agitated by a magnetic stirrer; 1.08% hydrogen was absorbed. The product was crystallized from ethyl acetate. Two crops, 0.74 and 0.7 g., were obtained, melting point 139–140°.

Conversion of *p*-Menthanetriol VIII to the Tribromide.—To the second crop of the above hydrogenated crystals 12.7 g. of a 40% hydrogen bromide solution in glacial acetic acid was added in a Pyrex weighing bottle. The solid was dissolved with shaking in about 15–30 minutes, but shortly after the whole mixture solidified to a purplish brown crystalline mass. Small pieces of ice were added, while cooling from the outside in ice water. The whole mixture was then filtered on a fritted glass funnel and the solids were washed with water, 4% sodium bicarbonate and again with water until neutral to litmus. The product was dried at 50° in vacuum. After two recrystallizations from isopropyl alcohol, it melted at 106–108°. Mixed melting point with an authentic (see below) 1,4,8-tribromo-*p*-menthane was 108.5°.

Preparation of 1,4,8-Tribromo-*p*-methane.—Anhydrous hydrogen bromide was passed into 100 g. of steam-distilled dipentene ($n^{20}{}_{D}$ 1.4728) in an all-glass apparatus which was cooled in a water-bath. After six hours, 113 g. of hydrogen bromide had been absorbed. The reaction mixture was almost completely solidified, white crystals in a purplish-brown liquid. The solid was triturated with cold methanol; weight of vacuum-dried product, 83.7 g. A small sample was recrystallized from ethanol, melting points 63–63.5°. Wallach gives melting point 64° for his "dipentene dihydrobromide."[18] The main product, without recrystallization, was brominated according to Wallach's procedure[10] which was improved by washing the crude tribromide crystals with ethanol, or recrystallizing from this solvent. The yield was low, 21.2 g., and the product melted at 108.5°.

Acknowledgment.—We are indebted to Professor C. C. Price of the University of Notre Dame for stimulating suggestions and to Eleanor I. Lansing for assistance in the experimental work. Dr. Evelyn Cook of this laboratory took the ultraviolet absorption readings.

Summary

1. The structure and the chemical behavior of the water-soluble products, obtained from terpinolene by oxidation with molecular oxygen in aqueous dispersion, were investigated.

2. It was shown that the three crystalline *p*-menthenetriols (m. p. 136, 124 and 121°, respectively) are new compounds and that even their hydrogenation products are different from the known menthanetriols.

3. Oxidation experiments (a) on the high-melting (136°) isomer with peracetic acid, followed by periodic acid titration of the resulting trihydric cineole, and (b) on both the menthenetriol and its hydrogenation product with chromic acid yielding "β-thujaketolactone" and "homoterpenyl methyl ketone," respectively, proved that the substance is a 3-*p*-menthene-1,2,8-triol.

4. The structure of the isomer melting at 124° was determined by two independent methods: (a) periodic acid oxidation followed by acid dehydration to yield acetone and *p*-cresol, and (b) hydrogenation followed by reaction with hydrogen bromide to yield Wallach's 1,4,8-tribromo-*p*-menthane, so that the compound must be a 2-*p*-menthene-1,4,8-triol.

5. A reaction mechanism based on resonance between two free radicals with alternative conjugated-double-bond systems is offered to explain the formation of the two triols.

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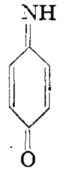
[18] Wallach, *Ann.*, **239**, 3 (1887).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quinone Imides. I. *p*-Quinone Disulfonimides

BY ROGER ADAMS AND A. S. NAGARKATTI[1]

p-Quinone mono- (I) and di-imines (II) were first prepared by Willstätter[2] by oxidation of *p*-aminophenol or *p*-phenylenediamine to the *p*-quinone monochloroimine or dichloroimine with bleaching powder followed by treatment of the products with hydrogen chloride. A more satisfactory procedure was oxidation of the appropriate aromatic amines in dry ether by means of dry silver oxide.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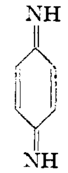
II

The products are colorless. They are very unstable to light, acids or in solution and polymerize with great ease. A characteristic property is the ease of hydrolysis to ammonia or amines and

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(1) An abstract of a thesis submitted by Mr. A. S. Nagarkatti to the Graduate College of the University of Illinois, 1949, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

(2) Willstätter and Mayer, *Ber.*, **37**, 1494 (1904); Willstätter and Pfannensteil, *ibid.*, **37**, 4605 (1904); **38**, 2244 (1905); Kehrmann and Cordone, *ibid.*, **56**, 2398 (1923); Cordone, *Helv. Chim. Acta*, **7**, 956 (1924).