2,3-Dimethylgalactose.—4,6-Benzylidene-2-methyl-β-methylgalactoside was boiled with 8% aqueous hydrochloric acid for three-quarters of an hour. The system was neutralized with barium carbonate, evaporated to dryness and the residue was extracted with acetone. When the solution was evaporated, a sirup was obtained. This product, on treatment with phenylhydrazine, yielded an osazone melting at 176–179°. A mixture of this compound and a specimen of 3-monomethylgalactosazone prepared by Robertson and Lamb[1] melted at the same temperature.

The authors wish to express their gratitude to Principal Sir James C. Irvine, D. Sc., LL.D., Sc.D., D.C.L., F.R.S., for his constant encouragement and kindly interest and advice.

Summary

The present paper describes the preparation and properties of 2-monomethylgalactose and 2,6-dimethylgalactose and their respective β-methylgalactosides. In addition, benzylidene-β-methylgalactoside and its methylated derivatives are described.

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[CONTRIBUTION FROM THE HERCULES POWDER COMPANY]

Oxidation in the Terpene Series. I. Action of Lead Tetraacetate and of Red Lead and Acetic Acid on Pinene, Dipentene, alpha-Terpinene and Terpinolene

BY KYLE WARD, JR.

The action of lead tetraacetate on the double bond has been studied by Criegee,[1] who found the product to be a mixture of acetates derived partly from the glycols obtained by hydroxylation of the double bond and partly from unsaturated alcohols in which a hydrogen in the beta-position to the double bond has been oxidized. In some cases dehydrogenation may occur, while in others the acetates are oxidized further to glycolic acid esters.

In Criegee's paper he predicted for the simpler terpenes a behavior similar to that of cyclohexene. However, his own findings show such marked differences in the behavior of different unsaturated compounds in this reaction that a study of the terpenes does not seem out of place. As will be seen later, his prediction holds good in a general way although the complex nature of the terpenes causes certain differences.

The present paper describes the general action of this reagent on four common terpenes: pinene, dipentene, alpha-terpinene and terpinolene. The main products, which are being further investigated, are shown to be acetates of mono-alcohols of the general formula $C_{10}H_{15}OH$ and of glycols of the formula $C_{10}H_{16}(OH)_2$.

To eliminate separate preparation and isolation of the lead tetraacetate, a modified procedure was investigated. The terpene was dissolved in acetic acid and oxidized by means of red lead. Here the lead tetraacetate formed from red lead and acetic acid may be expected to react at once with the terpene. Very similar products are formed in this way to those formed by the lead tetraacetate oxidation. The ratio of low-boiling to high-boiling acetates is much higher when lead tetraacetate is used, however, and there is some evidence that the products may differ in some cases, because the ester number of the higher-boiling acetate fraction is generally higher where lead tetraacetate is used. Such differences are to be expected because a number of factors differ where red lead and acetic acid are used. Some of these factors include the acidity of the solution, the introduction of water from the reaction of red lead and acid, and the presence of a solid phase with each addition of red lead.

Moreover, inactive sobrerol (pinol hydrate) was definitely identified as the main product from the oxidation of pinene with red lead and acetic acid, whereas it is obtained with lead tetraacetate only in acetic acid solution and then in low yield.

All of the esters, as well as the products obtained from them, are liquid, excepting the pinol hydrate previously mentioned. They are colorless or pale yellow in color and are usually very fragrant. The odor of lower esters resembles that of the esters of known terpene alcohols, such as bornyl and menthyl acetates. The higher esters have a much fainter odor.

The purpose of this preliminary work did not touch on the mechanism of the reaction, but there are a few points which may be mentioned, although further work must be done to clear them

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[1] Criegee, *Ann.*, **481**, 263 (1930).

up definitely. Criegee[1] already has pointed out a similarity between oxidation with lead tetraacetate and autoxidation, as well as oxidation with peracetic acid. In regard to the first, a difference may be pointed out, in that pinene, both with lead tetraacetate and with red lead and acetic acid, yields a tertiary acetate, whereas autoxidation gives verbenol, a secondary alcohol. The similarity is more marked as regards peracetic acid, because of formation of monoacetates of dihydric alcohols as well as diacetates, the ratio between the two varying with the solvent used. This agrees with the findings of Arbusov[2] and Böeseken[3] on the action of per-acids. Pinol, however, was not observed although the product was not specifically tested for its presence.

Acknowledgments are made to Hercules Powder Co. for permission to publish the material in this article and to Mr. E. A. Georgi of the Hercules Experiment Station for the microscopic identification of the pinol hydrate. This preliminary work is published as a unit carried out in the Hercules Experiment Station, but the author intends to investigate the unanswered questions more thoroughly as early as possible.

Experimental

Materials Used.—Ordinary powdered red lead and glacial acetic acid were used. Lead tetraacetate was prepared from this by the method of Dimroth[4] and recrystallized from benzene. The terpenes were prepared by redistilling the corresponding fractions[5] from steam-distilled wood turpentine. The boiling points of the materials used were:

Pinene	155–157° (alpha-Pinene)
Dipentene	175–177°
Terpinolene	185–187°
alpha-Terpinene	173–175°

While the pinene so obtained has a high degree of purity, the others probably contain isomers, because of their ease of isomerization. This point is relatively unimportant, as such isomerization undoubtedly occurs during the reaction also.

Oxidation with Lead Tetraacetate.—These oxidations were carried out in two ways: (1) by adding powdered lead tetraacetate to a solution of the terpene; or (2) by adding the terpene to a solution of lead tetraacetate. The latter is more convenient. Either benzene or acetic acid was used as a solvent. In a few runs, toluene was used, but unless the temperature is kept low this introduces the risk of contaminating the product with benzyl acetate.[4] The reaction of lead tetraacetate with the terpenes is strongly exothermic, so that, unless the addition be carried on very gradually, one must resort to external cooling. A convenient method is to add the terpene drop by drop to a refluxing solution of lead tetraacetate in benzene. Molecular equivalents of lead tetraacetate and terpene were used. The products obtained with benzene differ slightly from those obtained with acetic acid, as Criegee found, but nothing definite is available on this point yet.

The simplest method of working up the resulting product is to pour the reaction mixture into water and extract with benzene, ether or ethyl acetate, washing the extract free of lead with acetic acid. The solvent is then evaporated and the residue fractionated by vacuum distillation.

Oxidation with Red Lead and Acetic Acid.—Here the terpene was dissolved in the amount of acetic acid necessary for the preparation of a molecular equivalent of lead tetraacetate. The red lead was then added in small amounts. No heating is necessary as the reaction with the terpene soon raises the temperature. In fact, the rate of addition of red lead must be watched to prevent an uncontrollable reaction. Addition is continued until an excess of tetraacetate is present, as indicated by the formation of brown colloidal lead dioxide, on dilution with water. The product is worked up similarly to the product obtained with lead tetraacetate.

All four terpenes yield mixtures on oxidation by the aforementioned methods. These mixtures were separated by fractional distillation through a 12″ (30-cm.) Hempel column. Such distillation yields first a hydrocarbon fraction, which becomes too small for investigation if an excess of oxidizing agent is used. In the case of alpha-terpinene, this hydrocarbon fraction appears to be larger and unavoidable, but this is not certain.

The next fractions contain acetic acid esters of terpene alcohol. First come acetates of monohydric alcohols and then acetates (largely monoacetates) of dihydric alcohols.

The viscous residue above the decomposition point at 20 mm. absolute pressure (usually a little above 175°) has a lower saponification number than the preceding and is deep red to black in color. By using a Hickman still at 1 mm. pressure, a yellow oil of fairly high saponification number can be obtained, leaving a black, brittle residue.

All these fractions boil in roughly the same range regardless of the terpene oxidized. The table shows the range within which the amounts of the two main ester fractions may be varied.

TABLE I

Fraction, °C.	Mm.	Pinene, %	Dipentene, %	α-Terpinene, %	Terpinolene, %
100–135	20	21–64	10–45	19–51	15–62
135–175	20	23–52	23–71	32–55	25–71
Residue above 175	20	8–33	19–48	16–28	13–23

Unless otherwise noted, the following data refer to oxidations with red lead and acetic acid.

Hydrocarbon Fraction.—The fraction from oxidized pinene boiling below 100° at 20 mm. has an ester number of zero and n^{20}_{D} 1.4672. This would be expected for a hydrocarbon mixture.

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(2) Arbusov and Mikhailov, *J. prakt. Chem.*, **127**, 1 (1930).

(3) Böeseken and Schneider, *ibid.*, **131**, 285 (1931).

(4) Dimroth and Schweizer, *Ber.*, **56**, 1375 (1923).

(5) Obtained from the Hercules Powder Company.

From dipentene, the corresponding fraction has a very low ester number, 15 and $n^{20}\text{D}$ 1.4741. The fraction distils at 173–182° under atmospheric pressure. These figures would correspond to a mixture consisting essentially of monocyclic terpenes.

The hydrocarbon fraction from oxidized alpha-terpinene is slightly larger in amount than the others, but the work done with this hydrocarbon and with terpinolene is insufficient to justify any conclusions.

Esters of Monohydric Alcohols.—Table II compares the acetates from three of the four terpenes studied.

TABLE II

CONSTANTS OF THE LOWER ACETATES

	Pinene	Dipentene	α-Terpinene
B. p. at 20 mm., °C.	110–125	100–125	100–125
Sp. gr. 15.6°/15.6°	0.9914	1.0100	....
$n^{20}\text{D}$	1.4752	1.4810	1.5036
Ester number	267	241	275

The alcohols were prepared by saponifying these fractions with a solution of sodium hydroxide in dilute alcohol. The alcohols were recovered by dilution with water and extraction with ether.

Specifically, the alcohol from pinene boils at 110–115° at 20 mm. It is a tertiary alcohol, splitting off water with phenyl isocyanate to give diphenyl urea instead of a phenylurethan and with phthalic anhydride to give phthalic acid instead of an acid phthalate.

The alcohol from dipentene boils at 113–125° at 20 mm. Redistilled at atmospheric pressure, it shows three main fractions. About 30% comes over between 194–200°; after a gradual rise there is a large fraction, 55%, boiling 223–224° while about 10% boils at 235–242°.

The alcohol from terpinene boils 100–120° at 20 mm. Combustion shows it to have the formula $C_{10}H_{15}OH$.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.9, H, 10.6. Found: C, 78.9; H, 10.3.

The alcohol from terpinolene boils 102–125° at 20 mm.

Esters of Dihydric Alcohols.—Table III compares the second ester fractions of the three terpenes named.

TABLE III

CONSTANTS OF HIGHER ACETATE FRACTIONS

	Pinene	Dipentene	α-Terpinene
B. p. at 20 mm., ° C.	150–160	156–160	150–175
Sp. gr. 15.6°/15.6°	1.0593	....	....
$n^{20}\text{D}$	1.4747	1.4879	1.5033
Ester number	277	270	375

The theoretical ester number for the monoacetate of a terpene dialcohol $C_{10}H_{16}(OH)_2$ is 272, for the diacetate 451. It is obvious that the monoacetate of a dihydric alcohol of the formula given is not the only compound satisfying the above results. The following discussion of the individual products will explain the reasons for believing this to be the true explanation.

The saponification product obtained from pinene crystallizes on standing. Recrystallized from a little ether, it melted at 130–130.5° and was optically inactive. Pinol hydrate (inactive sobrerol) was prepared by a method of Wallach[6] which consists of treating terpineol dibromide with lead hydroxide. This melted at 129.5°; the mixed melting point was 130°. The material was also identified microscopically as inactive sobrerol.

The saponification product obtained from dipentene distils at 155–165° at 20 mm. (250–253° at 760 mm.) and analyzes as $C_{10}H_{18}O_2$. (Found: C, 69.8; H, 10.4. Calculated: C, 70.5; H, 10.7.) That both oxygens are present in hydroxyls, and adjacent hydroxyls, is shown by oxidation with lead tetraacetate. This yields a product, rather fruity in odor, which is probably a keto-aldehyde (the semicarbazone melts at 162°) as oxidation with chromic acid gives a keto acid (semicarbazone melts at 188–190°).

The saponified material from alpha-terpinene, distilling at 150–160° at 20 mm., also could be oxidized with lead tetraacetate, giving a very fragrant liquid (similar in odor to the corresponding material from dipentene or terpinolene) boiling at 124–127° at 20 mm.

The saponified material from terpinolene, which distils at 152–170° at 20 mm., was oxidized with lead tetraacetate, giving a fragrant liquid which can be further oxidized with chromic acid to give a liquid acid of pleasant odor. Titration corresponds to a monobasic acid of molecular weight 198. This is not in good agreement with the acid which might be expected here, which is 5-keto-2-isopropenylenanthic acid, molecular weight 184. It might be an oxidation or a hydration product of this acid, but further work is necessary before conclusions can be drawn.

High-Boiling Residue.—Distilled at 20 mm. pressure, the oxidation products of the terpenes begin to decompose at 175–190°. These high-boiling residues are deep red to black liquids, solidifying on cooling to resins. They show a decrease in ester number over the acetates of dihydric alcohols. On distilling at 1 mm. pressure, however, from a Hickman still, an appreciable fraction of rather high ester number comes over. Table IV shows the ester numbers of the original high-boiling residue and of the distillates therefrom.

TABLE IV

	Pinene	Dipentene	α-Terpinene
Ester number of original residues	222	181	...
Ester number of distillate therefrom	308	393	350

These fractions have not been investigated further.

Summary

1. The oxidation of the four terpenes: pinene, dipentene, alpha-terpinene and terpinolene by means of red lead oxide and acetic acid gives four main fractions, boiling at 20 mm. pressure at about: (a) 80–100° (hydrocarbon); (b) 115–130° (acetates of monohydric alcohols); (c) 150–175° (monoacetates of dihydric alcohols); (d) above 180° (probably polymerization products and higher acetates).

2. In the case of pinene, the dihydric alcohol produced by saponification of the acetate has been identified definitely as inactive sobrerol (m. p. 130–130.5°).

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(6) Wallach, *Ann.*, **277**, 115 (1893).