[CONTRIBUTION FROM THE HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

The Oxidation of Methyl Dehydroabietate by Molecular Oxygen

BY PAUL F. RITCHIE, THOMAS F. SANDERSON AND LANE F. MCBURNEY

RECEIVED FEBRUARY 12, 1953

The reaction between methyl dehydroabietate and molecular oxygen at 80° has been studied and the nature of the reaction products has been established. The major initial reaction product, methyl 9-hydroperoxydehydroabietate, has been isolated in crystalline form and its structure proved. Methyl 9-hydroxydehydroabietate and methyl 9-oxodehydroabietate have been prepared from the hydroperoxide. Catalytic reduction of the ketone resulted in formation of the epimeric methyl 9-hydroxydehydroabietate.

A number of workers have studied the absorption of oxygen by the resin acids[1] but only one of these researches resulted in characterization of reaction products. Drake,[2] who oxidized dehydroabietic acid with molecular oxygen in aqueous alkaline solution and in the presence of a persulfate catalyst, was able to show that 9-oxodehydroabietic acid is the chief product of that reaction. The same ketone was prepared by Pratt by oxidation of dehydroabietic acid with alkaline permanganate.[3]

The present authors have investigated the autoxidation and benzoyl peroxide-initiated oxidation of methyl dehydroabietate by molecular oxygen at atmospheric pressure and 80°. The low-melting methyl ester of dehydroabietic acid was chosen for oxidation since, by so doing, it was possible to avoid the complications introduced by the use of a solvent and to conduct the oxidations in the neutral organic medium of the molten ester. Oxidation was accomplished by continuous circulation of oxygen through the molten ester in a specially designed apparatus and the course of the reaction was followed by measuring the absorption of oxygen.

Results and Discussion

The autoxidation of methyl dehydroabietate (I) is characterized by a long induction period and follows a course which is typical of autocatalyzed reactions (Fig. 1, curve O). Addition of a small amount of benzoyl peroxide to the reaction mixture results in complete elimination of the induction period and the reaction appears to continue until 85 to 90 mole per cent. of oxygen has been absorbed. Examination of reaction mixtures obtained by oxidation in the presence of 2.4 mole per cent. of benzoyl peroxide revealed that, at extents of oxidation no greater than about 30 mole per cent., hydroperoxides are the exclusive products of the reaction. At higher extents of oxidation ketonic material, which has been shown to be methyl 9-oxodehydroabietate, appears in the reaction mixtures. In all cases the total of the amounts of hydroperoxide and ketone found in the mixtures is, within the errors involved in the analytical methods, equivalent to the oxygen absorbed.

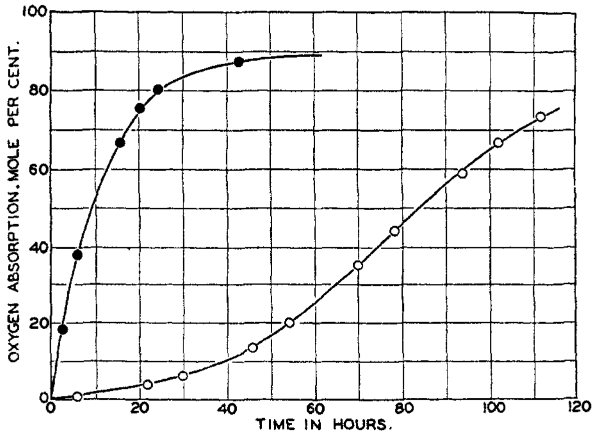


Fig. 1.—Oxidation of methyl dehydroabietate at 80°: O, autoxidation reaction; ●, oxidation in the presence of 2.42 mole per cent. of benzoyl peroxide.

The general method for isolating hydroperoxides, which involves precipitation of the salts by treating solutions of the mixtures in non-polar solvents with strong aqueous caustic,[4] failed when applied to the oxidates of methyl dehydroabietate. The hydroperoxide could, however, be isolated by countercurrent extraction of ketone-free oxidates using 90% methanol and hexane. The aqueous methanol solution thus obtained from an oxidate containing 29.8% of hydroperoxides yielded 9% over-all of crystalline monohydroperoxide of methyl dehydroabietate.

A priori it might be considered that either methyl 9-hydroperoxydehydroabietate (II) or methyl 14-hydroperoxydehydroabietate (III) would be the primary product of oxidation of methyl dehydroabietate by molecular oxygen. Oxidates were examined for the presence of methyl 14-hydroperoxydehydroabietate by a method which depends on recovery of the acetone formed upon treatment of the hydroperoxides of isopropylbenzenes (*e.g.*, α,α-dimethylbenzylhydroperoxide) with strong acids.[5] This method probably yields only semiquantitative results but indicates the presence of only 5 or 6 mole per cent. of methyl 14-hydroperoxydehydroabietate in mixtures resulting from extensive oxidation of methyl dehydroabietate. This evidence, together with that provided by Drake's and Pratt's earlier researches,[2,3] indicated that the crystalline hydroperoxide isolated is methyl 9-hydroperoxydehydroabietate. Unequivocal identification of the crystalline hydroperoxide as methyl 9-hydroperoxydehydroabietate was obtained by treatment of the hydroperoxide with aqueous methanolic ferrous sulfate to obtain methyl 9-oxodehydroabietate, saponification of the keto ester to the free acid and

---

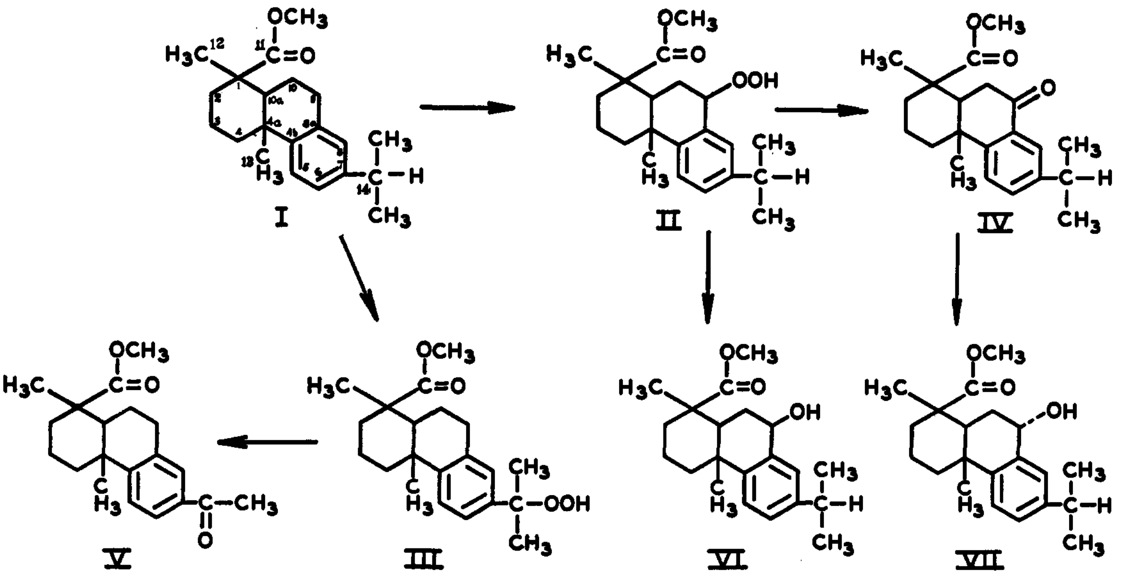
[1] *Inter alia;* S. S. Malevskaya and E. V. Kazeeva, *J. Applied Chem.* (*U.S.S.R.*), **21**, 854 (1948); D. Tishchenko, N. Komshilov, K. Kissel and S. S. Maelvskaya, *J. Gen. Chem.* (*U.S.S.R.*), **20**, 1225 (1950).

[2] A. E. Drake, U. S. Patent 2,434,643 (Jan. 20, 1948).

[3] Yolanda T. Pratt, THIS JOURNAL, **73**, 3803 (1951).

[4] H. Hock and S. Lang, *Ber.*, **76B**, 169, 1130 (1943).

[5] H. Hock and S. Lang, *ibid.*, **77**, 257 (1944); M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem*,. **15**, 748 (1950).



Methyl 9,α-hydroxy-dehydroabietate

Methyl 9,β-hydroxy-dehydroabietate

comparison of the product with an authentic specimen of 9-oxodehydroabietic acid.

Reduction of the hydroperoxide with sodium sulfide in aqueous methanolic solution resulted in almost quantitative formation of a crystalline methyl hydroxydehydroabietate. A second crystalline alcohol of the same empirical formula, but differing from the product of sodium sulfide reduction in melting point and rotatory power, was prepared by catalytic reduction of methyl 9-oxodehydroabietate in ethanolic solution over palladium. The crystalline 3,5-dinitrobenzoates prepared from the two alcohols had almost identical melting points but the melting point of a mixture of the two derivatives was depressed by at least 10°. Comparison of the X-ray diffraction patterns of the two dinitrobenzoates revealed that they are quite different compounds. It is clear, therefore, that the two alcohols are the epimeric methyl 9-hydroxydehydroabietates to which the configurations VI and VII have been arbitrarily assigned.

The authors wish to express their gratitude to Dr. E. V. Cook of the Spectroscopy Laboratory at the Hercules Experiment Station for valuable assistance during the course of this research.

Experimental Details

Apparatus and Materials. Oxidation Apparatus.—The all-glass apparatus employed in studying the reaction was a modified version of one previously described in the literature.[6]

Methyl Dehydroabietate.—The preparation of methyl dehydroabietate was accomplished by a method which has been developed in these laboratories. The product obtained by methylating rosin was dehydrogenated over a palladium catalyst at 260° to obtain a mixture which contained 50 to 60% of methyl dehydroabietate. Fractional distillation of the dehydrogenation product was followed by the ultraviolet spectrophotometric method (methyl dehydroabietate, $\lambda^{\text{EtOH}}_{\text{max}}$ 275.7 mμ, α 2.46) and the fractions rich in methyl dehydroabietate were crystallized from methanol to a constant melting point (62.5 to 63°). Prior to use the crystals were dried overnight at 50° in a vacuum oven.

Benzoyl Peroxide.—Commercial benzoyl peroxide (Eastman Kodak Company, Eastman Grade) was purified according to Gatterman.[7] The crystals were dried in a vacuum desiccator overnight at 0.3 mm. pressure and melted at 107 to 108°.

Experimental Procedures.[8] Oxidation of Methyl Dehydroabietate.—The technique of oxidation is illustrated by the following experiment. A sample of 10.0 g. of methyl dehydroabietate and 0.186 g. (2.42 mole per cent.) of benzoyl peroxide was weighed into the reaction cell and the cell connected into the circulating system. Air was removed from the system by flushing three times with dry oxygen and the buret was filled with oxygen. The oil-bath, which had been heated previously to 80°, was raised under the reaction cell. After liquefaction of the methyl dehydroabietate (2 to 3 minutes), the pressure in the system was adjusted and circulation of oxygen begun. Absorption of oxygen was followed by periodic reading of the gas buret. The data thus obtained are recorded in Fig. 1 (curve o). After 43 hours 623 ml. (S.T.P.) of oxygen had been absorbed and reaction was essentially complete. The oxidate contained 56% of hydroperoxides and 25% of methyl 9-oxodehydroabietate.

Hydroperoxide Analyses.—Mixtures containing hydroperoxides were analyzed by the method described by Wagner, Smith and Peters.[9] Hydroperoxide contents of all mixtures were calculated on the assumption that only monohydroperoxides of methyl dehydroabietate were present.

Determination of Methyl 9-Oxodehydroabietate.—Mixtures containing methyl 9-oxodehydroabietate were analyzed by the ultraviolet spectrophotometric method.

Detection of Tertiary Hydroperoxides.—The following experiment is illustrative of the technique used to determine tertiary hydroperoxides. A sample of ester (7.2 g.) was oxidized in the presence of 0.134 g. of benzoyl peroxide. After 29 hours the oxidate had absorbed 85.6 mole per cent. of oxygen and contained 56% of hydroperoxides and 24% of methyl 9-oxodehydroabietate. The oxidate was decomposed at 70° with 0.5 g. of trichloroacetic acid, and the volatile products were passed into an aqueous solution of 2,4-dinitrophenylhydrazine by means of a nitrogen stream. The precipitation of an orange-yellow dinitrophenylhydrazone began immediately and was complete in 1.5 hours. After isolation and drying the crude product weighed 0.219 g. and melted between 121 and 123°. After recrystallization the dinitrophenylhydrazone melted between 124.5 and 126° and showed no depression in melting point when mixed

---

[6] L. F. McBurney, *Ind. Eng. Chem.*, **41**, 1251 (1949); E. F. Evans and L. F. McBurney, *ibid*, **41**, 1260 (1949).

[7] L. Gatterman "Laboratory Methods of Organic Chemistry," The Macmillan Co., Ltd., London, 1941, p. 125.

[8] Melting points are corrected. Analyses were performed by the Analytical Division of the Hercules Experiment Station.

[9] C. D. Wagner, R. H. Smith and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

with an authentic sample of the 2,4-dinitrophenylhydrazone of acetone.

Methyl 9-Hydroperoxydehydroabietate.—Methyl dehydroabietate (40.0 g.) was oxidized in the presence of 2.00 g. of benzoyl peroxide. Reaction was allowed to continue until 30.0 mole per cent. of oxygen had been absorbed. The product contained 29.8 mole per cent. of hydroperoxide. Fractionation of the oxidate was accomplished by discontinuous countercurrent extraction in separatory funnels using hexane and methanol containing 10% of water as the solvent pair. The method involves the diamond pattern of phase combination which has been described fully by Bush and Denson.[10] The fraction recovered from hexane (29.0 g.) contained 3.4% of hydroperoxide and yielded 21.3 g. of unchanged methyl dehydroabietate upon crystallization from methanol. After combination, the methanol solutions were poured into water and the precipitated material recovered by ether extraction. The ether-soluble fraction weighed 12.2 g. and contained 82.8% of hydroperoxide. Crystallization from methanol gave 3.6 g. of slender needles having a m.p. of 132.5 to 133.5°, $[\alpha]^{24}\text{D}$ −14° (1%, ethanol). *Anal.* Calcd. for $C_{21}H_{30}O_4$: C, 72.85; H, 8.75; active oxygen, 4.62. Found: C, 72.80; H, 8.73; active oxygen, 4.60.

Methyl 9-Oxodehydroabietate.—A ferrous sulfate solution (1.8 g. in 40 ml. of a 1:1 water–methanol solution) was added dropwise with agitation to a solution of 9-hydroperoxydehydroabietate (1.0 g. in 50 ml. of methanol) over a period of one hour. The reaction mixture was heated to 50° and stirring continued for 1.5 hours. Several volumes of water were added to the reaction mixture and the precipitated material recovered by extraction with ether. The ether soluble fraction weighed 0.96 g. and after flash distillation at 0.2 mm. pressure the distillate weighed 0.78 g. After recrystallization from aqueous methanol the product melted at 68 to 69°, $[\alpha]^{24}\text{D}$ +6.4° (2%, ethanol), $\lambda_{\max}^{\text{EtOH}}$ 254 mμ, α 35.5. *Anal.* Calcd. for $C_{21}H_{28}O_3$: C, 76.80; H, 8.59. Found: C, 76.74; H, 8.75. A 2,4-dinitrophenylhydrazone was prepared and crystallized to constant melting point from ethanol, m.p. 184.5 to 185.5°. *Anal.* Calcd. for $C_{27}H_{32}O_6N_4$: N, 11.01. Found: N, 11.37. A sample (0.5 g.) of the ketone was saponified by heating under reflux for 2 hours with 0.2 g. of sodium hydroxide dissolved in 25 ml. of diethylene glycol and 1 ml. of water. The product was recovered and recrystallized to constant melting point (159.5–161°) from aqueous methanol. The mixed melting point of the material and a sample of 9-oxodehydroabietic acid[11] was unchanged. The X-ray diffraction patterns of the two specimens were identical.

Methyl 9-Hydroxydehydroabietate.—A solution of sodium sulfide (1.5 g. in 50 ml. of a 1:1 water–methanol solution) was added dropwise with agitation to 1.5 g. of 9-hydroperoxydehydroabietate in 50 ml. of methanol over a period of two hours. The reaction mixture was heated and stirred at 50° for 3 hours before adding water and extracting the product with ether. The ether extract was recrystallized from aqueous methanol to yield 1.43 g. of material melting between 103–105°, after recrystallization the white needles melted from 112 to 112.5°, $[\alpha]^{24}\text{D}$ +17° (1%, ethanol). *Anal.* Calcd. for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15. Found: C, 76.74; H, 9.41. A 3,5-dinitrobenzoate was prepared and crystallized from ethanol to constant melting point (163.5 to 164.5°). *Anal.* Calcd. for $C_{28}H_{32}O_8N_2$: N, 5.34. Found: N, 5.30. A sample of the methyl 9-hydroxydehydroabietate (0.40 g.) was saponified by heating under reflux in 15 ml. of diethylene glycol containing 0.15 g. of potassium hydroxide for 3 hours. The free acid was recovered and crystallized to constant melting point (178.5 to 179.5°) from a mixture of benzene and hexane. Calcd., neut. equiv., 316; found, neut. equiv., 316.

A sample (0.70 g.) of methyl 9-oxodehydroabietate was reduced with hydrogen in ethanolic solution at room temperature using 0.60 g. of palladium catalyst. The sample rapidly absorbed 1 mole per mole of hydrogen and the reduction was terminated at this point. After removal of the catalyst the product (0.61 g.) was recovered by evaporation of the solvent. The product was dissolved in 25 ml. of pyridine containing 1.0 g. of succinic anhydride and the resulting solution heated under reflux for 2 hours. The pyridine was removed under reduced pressure and the residue dissolved in ether. The acidic material was isolated by extraction with 2% potassium carbonate solution. After neutralization, the carbonate solution was extracted with ether. The hydrogen succinate was obtained by removal of the ether and saponified by heating under reflux for 30 minutes with 25 ml. of methanol containing 1 g. of potassium hydroxide. The product was precipitated by addition of water and extracted with ether. After crystallization from isoöctane there was obtained 0.42 g. of heavy prisms which were recrystallized from the same solvent to constant melting point, m.p. 92 to 93°, $[\alpha]^{24}\text{D}$ +56° (1% ethanol). *Anal.* Calcd. for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15. Found: C, 76.56; H, 9.29. A 3,5-dinitrobenzoate was prepared from the alcohol and crystallized from ethanol to constant melting point (163–164°). On admixture of this dinitrobenzoate with that prepared from the alcohol melting at 112–112.5° the melting point was depressed to 149–152°. The X-ray diffraction patterns of the two dinitrobenzoates were distinctly different.

WILMINGTON, DELAWARE

---

[10] M. T. Bush and P. M. Denson, *Anal. Chem.*, **20**, 121 (1948).

[11] A sample of 9-oxodehydroabietic acid was provided by Dr. Yolanda T. Pratt of the University of Maryland.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Correlation of Carbohydrate Structure with Papergram Mobility[1,2]

BY DEXTER FRENCH AND GENE M. WILD

RECEIVED DECEMBER 12, 1952

The regularity of the papergram mobilities of homologous oligosaccharide series leads to a straight line characteristic for each series when the logarithm of a partition function, α′, is plotted against molecular size. The partition function is obtained from single or multiple ascent papergrams. These observations can be correlated into the generalization that increasing the size of a saccharide by one hexose unit will decrease the papergram mobility by an amount which depends on the type of hexose unit being added and on its mode of attachment. Examples given include oligosaccharides of the starch, dextran, levan, inulin and galactan types.

In a previous publication[3] it was observed empirically that the papergram mobilities of the starch series of oligosaccharides fall into a regular series, such that on plotting the logarithm of the apparent R_f (from multiple ascent development) against the molecular size a curve was obtained which approached a straight line at low R_f values. Oligosaccharides of the dextran series were found to fall on a similar curve of greater slope, while the presence of a single 1,6-link in an otherwise 1,4-linked saccharide decreased the logarithm of the mobility by a fairly constant amount. These observations have been used in this Laboratory in an empirical way to infer structural relationships between saccharides.[4] Development of the theory of paper

---

[1] Journal Paper No. J-2202 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project 1116.

[2] Presented before the Division of Sugar Chemistry of the American Chemical Society, April, 1952.

[3] D. French and D. W. Knapp, *J. Biol. Chem.*, **187**, 463 (1950).

[4] D. French, *Science*, **113**, 352 (1951).