A sample crystallized twice from methanol had m.p. 125°.

Anal. Calcd. for $C_9H_6Cl_4O_2$: C, 37.54; H, 2.10; Cl, 49.25. Found: C, 36.93; H, 2.45; Cl, 49.14. Found for a second sample: C, 37.14; H, 3.03; Cl, 48.52.

The mother liquors from the above were distilled, b.p. 140–146° at 80 μ, yield 15.8 g. This product was redistilled at 60 μ, yielding the following fractions: (1) b.p. 132–135°, 0.95 g.; (2) b.p. 135–138°, 7.0 g.; (3) b.p. 138°, 4.6 g. Fractions 2 and 3 both showed absorptions in the hydroxyl and ether regions of the infrared.

Anal. Found for Fraction 2: C, 35.27, 35.21; H, 2.92, 3.02; Cl, 50.32. Found for Fraction 3: C, 34.89, 34.92; H, 2.50, 2.51; Cl, 50.69.

The above oil (7 g.; half from Fraction 2 and half from Fraction 3 was dissolved in pyridine (40 ml.) and acetic anhydride (15 ml.), and the solution was left standing at room temperature for 5 days. The reaction mixture was taken up in a large volume of benzene and extracted three times with water. The benzene layer was dried over magnesium sulfate. Removal of the solvent gave the crude product (III); yield, 3.2 g., m.p. 103–107°. After five crystallizations from hexane the melting point was 119–120°. This product shows a melting point depression both with the acetate of I and with II.

Anal. Calcd. for $C_{11}H_9O_3Cl_5$: C, 36.05; H, 2.48; Cl, 48.38. Found: C, 35.37, 35.48; H, 2.36, 2.48; Cl, 48.03, 48.14.

Pentachlorobenzene. Sodium (6.9 g., 0.3 g.-atom) was allowed to react with methanol (500 ml.). Pentachlorobenzaldehyde (13.9 g., 0.05 mole) was added and the solution was refluxed 65 hr. Half of the methanol was removed by distillation, water was added, and the mixture was extracted three times with benzene. The benzene solution was dried over magnesium sulfate. Removal of the benzene gave the crude product which was crystallized from ethanol; yield, 6.2 g. (49.6%), m.p. 84–85°.

Anal. Calcd. for C_6HCl_5: Cl, 70.81. Found: Cl, 71.34, 70.33.

Pentachloroacetophenone treated as above gave the same product in 50.4% yield.

NORTH ADAMS, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Reactions of Terpenes. IV.[1] Reaction of α-Pinene Oxide with p-Toluenesulfonic Acid and Quinaldine

L. CARROLL KING AND HUGH FARBER[2]

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When α-pinene oxide in quinaldine solution is treated with catalytic amounts of p-toluenesulfonic acid, about 30% of the oxide is converted to a mixture of aldehydes. The remainder of the α-pinene oxide is converted to a mixture of hydrocarbons. The aldehyde fraction consists of α-campholenic aldehyde, 85%, and a new aldehyde identified as 2,2,4-trimethyl-3-cyclopentene-1-acetaldehyde. The hydrocarbon fraction consists of four components. One of these is p-cymene and two others can be isomerized to p-cymene.

All former preparations wherein "α-campholenic aldehyde" was reported as the product of action of acid catalysts on α-pinene oxide are shown to be mixtures consisting of α-campholenic aldehyde as described herein, and 2,2,4-trimethyl-3-cyclopentene-1-acetaldehyde.

When α-pinene oxide in quinaldine solution is treated with catalytic quantities of p-toluenesulfonic acid, 30% of the α-pinene oxide is converted to aldehydes (Fraction I) and about 70% of the α-pinene oxide is converted to hydrocarbons (Fraction II).

The aldehyde fraction (I) was separated from the hydrocarbon fraction (II) by formation of the water soluble bisulfite adducts, and subsequent decomposition with sodium hydroxide. This fraction formed a derivative, m.p. 137–139°, when treated with semicarbazide, and corresponds to "α-campholenic aldehyde" as reported in the terpene literature.[3,4,5,6,7]

When Fraction I was subjected to analysis by gas chromatography the presence of two substances was indicated. The faster moving component represented 15% of the total aldehyde fraction and was identified as 2,2,4-trimethyl-3-cyclopentene-1-acetaldehyde (III). The slower moving component representing 85% of the aldehyde fraction has the structure IV.

In the terpene literature structure IV has been assigned to "α-campholenic aldehyde," the aldehyde produced when α-pinene oxide is treated with acid catalytists.[3,4,5,6] In view of the results described herein we conclude that all former preparations wherein "α-campholenic aldehyde" was prepared by the action of acid catalysts on α-pinene oxide are mixtures consisting of III and IV in the ratio of about 3:17. As a check on this statement "α-campholenic aldehyde" was prepared by the method of Royals and Harrell.[5] This preparation when treated with semicarbazide hydrochloride provided a derivative, m.p. 137–139°, as reported.[5] When examined by means of

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(1) Paper No. III, L. C. King and E. W. Stern, *J. Org. Chem.*, **23**, 1928 (1958).

(2) From the Ph.D. thesis of Hugh Farber, Northwestern University, 1959.

(3) B. A. Arbuzov, *Ber.*, **68**, 1430 (1935).

(4) B. A. Arbuzov and E. G. Isaeva, *Zhur. Obshchei Kim.*, **24**, 1250 (1954).

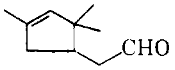
(5) E. E. Royals and L. L. Harrell, Jr., *J. Am. Chem. Soc.*, **77**, 3405 (1955).

(6) N. Prileshajew and V. J. Wershuck, *J. Russ. Phys. Chem. Soc.*, **61**, 445–465.

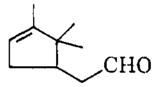
(7) Technical Bulletin No. 82, Becco Chemical Division, Food Machinery and Chemical Corp., Buffalo, N. Y.

gas chromatography this preparation as expected was a mixture of III and IV in the ratio of 3:17.

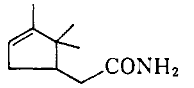
The properties of α-campholenic aldehyde (IV), homogeneous as estimated by gas chromatographic analysis are described for the first time in this paper.



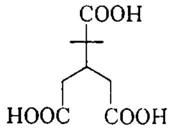
III



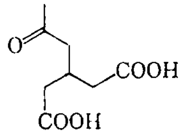
IV



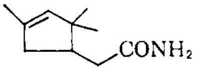
V



VI



VII



VIII

For purposes of structure investigation and derivative preparation the aldehyde fraction (I) was separated into its components, III and IV, by means of gas chromatography. In addition it was possible to obtain both III and IV 95% pure by repeated fractionation using an efficient column.

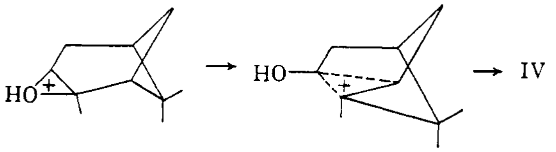
Characterization of IV. On oxidation with silver oxide followed by conversion to the amide, compound IV was converted to α-campholenamide V; $[\alpha]^{29}_{D}$ 7.92, m.p. 125.5–126.5°. Recently Walling and Buckler[8] prepared α-campholenamide V from the oxime of d-camphor using the method of Behal[9] and reported a melting point of 130–130.2°. Other workers have reported a variety of melting points for V.[10] In view of this situation with respect to the properties of V it seemed desirable to verify the structure IV by other means.

On ozonization followed by hypobromite decomposition of the ozonide,[11] α-campholenic aldehyde IV was converted to isocamphoronic acid (VI), m.p. 166–167°, in agreement with the compound as prepared by Tiemann and Semmler,[12] and synthesized by Perkin.[13] In addition IV was ozonized and the ozonide decomposed by chlorine[11] to give isoketocamphoric acid (VII), m.p. 131°.[12] This series of degradation products are best interpreted in terms of the structure IV for α-campholenic aldehyde.

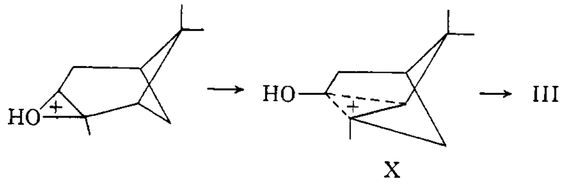
Physical constants and other functional derivatives for IV are described in the experimental part.

Characterization of III. The aldehyde III is an isomer of IV. On silver oxide oxidation of III followed by conversion to the amide, compound III gave VIII, an amide isomeric with V. On ozonization of III, followed by hypobromite decomposition[11] of the ozonide, isocamphoronic acid (VI) was obtained. This series of observations can be accommodated by the structure III. Compound III was further characterized by physical constants and certain functional derivatives. These are described in the experimental part.

On mechanistic grounds the formation of both III and IV when α-pinene oxide is treated with a nonnucleophilic Lowry-Bronsted acid[14,15] should be expected. Thus the formation of α-campholenic aldehyde IV from α-pinene oxide can be visualized as initial attack of a proton on the oxide ring followed by rearrangement of the *gem*-dimethyl group to form a camphane type carbonium ion (IX). The ion IX might then collapse to IV returning the catalytic proton to the solvent quinaldine. The same general mechanistic features can be visualized in connection with the formation of III. That is, initial attack of a proton on the oxide ring followed by rearrangement of the methylene group to form a cyclic fenchane type of carbonium ion (X). This ion can collapse with loss of proton to form III. The terpene literature has numerous examples of cases wherein pinene on treatment with acids is converted to fenchane derivatives.[16]



IX



X

EXPERIMENTAL[17,18]

Reaction of α-pinene oxide with quinaldine and p-toluenesulfonic acid. α-Pinene oxide, 30 g., was added to 100 cc. of quinaldine containing 1.0 g. of p-toluenesulfonic acid. This

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[8] C. Walling and S. A. Buckler, *J. Am. Chem. Soc.*, **77**, 6039 (1955).

[9] M. A. Behal, *Bull. Soc. Chim.* (3), **13**, 834 (1895).

[10] Walling and Buckler (Ref. 8) reported m.p. 138–141° for V, prepared from α-campholenic acid isolated from thermal decomposition of the hydroperoxides obtained by oxidation of d-bornyl chloride Grignard reagent.

W. A. Mosher and E. O. Langerak, *J. Am. Chem. Soc.*, **73**, 1302 (1951) reported m.p. 121–122° for V prepared from α-campholenic acid isolated from chromic acid oxidation of isoborneol.

Others have reported m.p. 125°, A. Ganadini, *Gazz. chim. ital.*, **72**, 131 (1942); and m.p. 124°, F. W. Tiemann, *Ber.*, **30**, 246 (1897).

[11] L. C. King and H. Farber, 136th Meeting of the American Chemical Society, Atlantic City, N. J., 1959, Abstracts of Papers, 89 p.

[12] F. Tiemann and F. W. Semmler, *Ber.*, **29**, 529, 3014 (1896).

[13] W. H. Perkin, *J. Chem. Soc.*, **81**, 246 (1902).

[14] T. M. Lowry, *Chemistry and Industry*, **42**, 43 (1923).

[15] J. N. Bronsted, *Rec. Trav. Chim.*, **42**, 718 (1923).

[16] J. L. Simonsen, *The Terpenes.*, Vol. II, second ed., pp. 552–554, Cambridge University Press (1949).

[17] Analysis by H. Beck.

[18] All melting points were observed on a Fisher-Johns block.

reaction mixture was heated for 8 hr. on the steam bath. The neutral reaction products were separated by addition of ether, and washing the ether solution with dilute hydrochloric acid. On evaporation of the ether an oil remained. This oil was separated into an aldehyde fraction (Fraction I) and a hydrocarbon fraction (Fraction II).

Fraction I. The oil described above was shaken with an excess of saturated sodium bisulfite solution, diluted with water and extracted with ether. The water soluble adduct was separated and the aldehydes regenerated by treatment with 10% sodium hydroxide. The aldehyde fraction after vacuum distillation was a water white oil and was identified as Fraction I; yield 9.0 g., 30%, based on α-pinene oxide.

This fraction formed a semicarbazone, m.p. 137–138°, and was tentatively identified as "α-campholenic aldehyde."

On analysis by analytical gas chromatography,[19] Fraction I was shown to be a two component mixture. The faster moving component III, representing 15% of the mixture, was eluted in 18 min. The slower moving component IV, 85% of the mixture, was eluted 24 min. after being placed on the column.

Fraction II. After separation of Fraction I, the ether soluble material was isolated by evaporation. The crude product was brown but on vacuum distillation gave a water white material, yield 15 g. This oil was identified as Fraction II. This fraction was examined by gas chromatography[19] and shown to be a four-component mixture. The elution times and relative amounts of the four materials are shown in the following table.

Time, Min.[a]	% of Total	% of Total after H_2SO_4 Treatment
8	39	13.5
10	19.5	48
13	30	14
16.5	12	27

[a] Represents maximum of elution peak.

The substance eluted in 10 min. was shown to be *p*-cymene by comparison with an authentic sample which was eluted in 10 min. at the same conditions.[19]

The above hydrocarbon fraction was treated with catalytic quantities of dilute sulfuric acid for 15 min. whereupon the *p*-cymene content increased.

Preparation of pure III *and* IV. Fraction I when subjected to careful fractionation[20] could be separated into a fraction, b.p. 70–71.5°, 10.5 mm., and a fraction, b.p. 72–74°, 10.5 mm. By gas chromatography analysis,[19] the lower boiling fraction was 95% III and 5% IV, whereas the higher boiling fraction was 95% IV and 5% III. These preparations were used for some of the degradation work described below.

Pure samples of III and IV were obtained by means of preparative gas entrained chromatography.

The column used for separation of chromatographically pure aldehydes III and IV consisted of a pyrex tube of $^5/_8$ inch inside diameter, 6 feet in length and was packed with tricresyl phosphate absorbed on powdered firebrick. This column was enclosed in a brass jacket to which was attached nichrome wire for heating the column. The temperature was controlled at the head, at the pot, and along the column proper. This assembly was in turn enclosed in an asbestos jacket. Nitrogen was used as the carrier gas and part of the eluted sample was shunted through a detector which in turn was connected to a Brown recorder. A four position stopcock was used to direct each fraction to different receivers.

Separation into the pure components could be effected with no center fraction on samples of 0.3 cc. With larger samples there was some trailing of the first fraction into the second. Typical conditions for a run might be as follows. Fraction I, 0.3 cc., was added to the column with nitrogen as a carrier gas under a pressure of 20 mm. with temperatures of 178° at the head, 165° in the middle of the column, and 85° at the bottom where the sample was eluted. The flow rate was 330 cc. per minute and elution times of 12 and 15 min. were observed for the two materials.

The fractions isolated by means of the above procedures were characterized as follows: *2,2,4-Trimethyl-3-cyclopentene-1-acetaldehyde,* III. Elution time on the preparative column 12 min., n_D^{29} 1.4578, $d^{25.5}$ 0.9075, b.p. 70–71.5° at 10.5 mm.[21]

Semicarbazone of III was crystallized from ethyl acetate pentane, m.p. 125–126°.

Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.13; H, 9.15. Found: C, 63.17; H, 8.95.

Dimedon derivative of III. This preparation appeared to be a mixture. The mixture on treatment in 80% methanol with catalytic amounts of sulfuric acid gave the octahydroxanthene derivative[22]; m.p. 154–155° after crystallization from water-methanol.

Anal. Calcd. for $C_{26}H_{36}O_3$: C, 78.76; H, 9.15. Found: C, 78.89; H, 9.23.

2,2,4-Trimethyl-3-cyclopentene-1-acetamide VIII *from* III. A suspension of 0.15 g. (0.001 mole) of III and 0.37 g. (0.0015 mole) of silver oxide in 10 cc. water with 3 cc. of 10% sodium hydroxide was stirred at 35° for 1 hr. Filtration afforded a clear yellow solution which on acidification and ether extraction yielded a small quantity of yellow oil. This oil on treatment with thionyl chloride, and subsequently with ammonia, formed a yellow precipitate. Filtration afforded 70 mg. of solid (50% based on aldehyde used) melting over a 10° range. Recrystallization three times from ethyl acetate–pentane afforded white crystals melting at 85–86°, $[\alpha]_D^{29}$ 15.3°.

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.25. Found: C, 71.48; H, 10.13.

Degradation of III *to isocamphoronic acid,* VI. A solution of 0.78 g. (0.005 mole) of III in 40 cc. of pentane at −13° was ozonized. After completion of the ozonization the pentane solution was placed in a 500 cc. Erlenmeyer flask and the viscous, pentane insoluble, ozonide was washed from the ozonization tube with acetone and added to the flask. The solvents were removed under vacuum and the residual ozonide was treated with cold potassium hypobromite solution.[23] The ozonide was allowed to react with the hypobromite for 12 hr. at 0° and 4 hr. at 40°; during this process carbon tetrabromide, m.p. 89°,[24] collected on the sides of the flask.

The solution was filtered and the filtrate acidified and evaporated to dryness. Ether extraction of the dried filtrate resulted in the isolation of 0.79 g. (73%) of crude isocamphoronic acid melting at 145–155°. Recrystallization from ether-chloroform solution with Norite "A" treatment yielded white crystals melting at 164–166°.

Anal. Calcd. for $C_9H_{14}O_6$: C, 49.54; H, 6.47. Found: C, 49.88; H, 6.66.

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(19) Analytical gas chromatography column data. Length, 1.8 m.; packing, tricresyl phosphate on fire brick; temperature, 130–131°; carrier gas, helium at 8.5 p.s.i.

(20) Using a Podbielniak spinning band column and operating at 10 mm.

(21) Boiling point measurements represent still head temperatures on 95% pure III or IV.

(22) W. Weinberger, *Ind. Eng. Chem., Anal. Ed.,* **3,** 365 (1931). E. C. Horning and M. G. Horning, *J. Org. Chem.,* **11,** 95 (1946).

(23) Potassium hydroxide (33.6 g.) in 180 cc. of water was treated with 33 g. of bromine keeping the temperature at 0°.

(24) Lang, *Handbook of Chemistry,* 8th ed., Handbook Publishers, Inc., p. 432.

α-Campholenic aldehyde, IV. This substance was characterized as follows: Elution time from preparative column 15 min., n_D^{29} 1.4644, $d^{25.5}$ 0.9235, b.p. 72–74°, 10.5 mm.[22]

Semicarbazone of IV. Compound IV, (0.15 g., 0.001 mole) 0.12 g. of semicarbazide hydrochloride, and 0.10 g. of sodium acetate were dissolved in 80% aqueous ethanol and heated at 80° for 15 min. Addition of water and cooling, followed by filtration and drying, yielded 0.20 g. of solid (95% based on aldehyde used) with a melting range of 130–145°. Recrystallization from ethyl acetate–ligroin solution with slow cooling resulted in the isolation of two crystalline forms. One of the forms was fine needles melting at 154–155° and the other was rather amorphous and melted over the range 130–145°. The infrared spectra of the two forms in solution were identical. The material melting at 154° was analyzed.

Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.13; H, 9.15. Found: C, 63.17; H, 9.42.

Dimedone derivative of IV. Fifty milligrams of IV (0.00033 mole) in 2.5 cc. 50% aqueous ethanol was treated with 150 mg. of dimedone (0.001 mole) with a drop of piperidine as catalyst. After refluxing for 5 min. and cooling a white crystalline mass was isolated. This was crystallized twice from absolute methanol, m.p. 147–147.5°, (mixed melting point with dimedone as 128–137°).

Anal. Calcd. for $C_{26}H_{38}O_4$: C, 75.32; H, 9.21. Found: C, 75.77; H, 9.10.

Octahydroxanthene derivative of IV. One hundred milligrams of the dimedone derivative from IV, in 3 cc. 80% methanol, was treated with a drop of concd. sulfuric acid at the boiling point of the solvent for 15 min. Cooling afforded white crystals which crystallized from methanol, m.p. 168–169°.

Anal. Calcd. for $C_{26}H_{36}O_3$: C, 78.76; H, 9.15. Found: C, 78.44; H, 8.97.

Preparation of α-campholenamide V *from* IV. A suspension of 1.5 g. (0.01 mole) of IV and 3.7 g. (0.015 mole) silver oxide–water in 20 cc. of 10% sodium hydroxide at 40° was stirred vigorously for 3 hr. At the end of this time a heavy silver mirror had formed and black colloidal silver was present. Filtration afforded a pale yellow solution which when acidified with dilute hydrochloric acid yielded a pale yellow oil. This oil on treatment with thionyl chloride and subsequently with ammonia gave a yellow solid. Crystallization twice from ethyl acetate-pentane solution, followed by sublimation at 1 mm., gave 0.6 g. (36%) of V, m.p. 124.5–126°, $[\alpha]_D^{29}$ 7.2.

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.25. Found: C, 72.07; H, 10.31.

Preparation of isoketocamphoric acid VII *from* IV. Compound IV, 1.3 g. (0.008 mole), was dissolved in 40 cc. absolute methanol and ozonized at −70°. After ozone uptake ceased, the solution was diluted with 30 cc. water and about 3 g. of chlorine was passed into this mixture maintaining the temperature at 0°. The solution was allowed to stand at 5° for 12 hr. and was then diluted with 100 cc. water and extracted five times with ether. The ether extracts were washed twice with 50-cc. portions of water and then dried over sodium sulfate. Evaporation of the ether yielded a light tan oil which when treated with sodium hydroxide slowly dissolved in the aqueous solution. Acidification with concentrated hydrochloric acid followed by ether extraction, yielded 0.9 g. (50%) of ether soluble solid. Crystallization from chloroform-pentane, afforded 0.74 g. of dry acid, m.p. 128–130°. Recrystallization from chloroform-pentane solution raised the melting point to 130–131°, lit.[12,13] m.p. 129–130°; neut. equiv., calcd. 108.12, found, 109.

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.55; H, 7.55. Found: C, 55.99; H, 7.34.

Degradation of IV *to isocamphoronic acid* VI. Compound IV, 1.5 g. (0.01 mole) in 40 cc. of pentane at −15° was ozonized until ozone uptake ceased. The resulting pentane solution was placed in a 500 cc. Erlenmeyer flask and the viscous, pentane insoluble ozonide was washed from the ozonizing tube with acetone and added to this flask. The solvents were removed under vacuum and a very viscous clear oil remained. To this oil was added a prepared solution of potassium hypobromite.[23] The reaction mixture was maintained at 0° for 12 hr. and then at 40° for 4 hr. The reaction mixture was filtered, acidified, and evaporated to dryness. Extraction with ether yielded 1.44 g. (67% based on aldehyde) of crude isocamphoronic acid, m.p. 150–160°. Recrystallization three times from ether-chloroform solution raised the melting point to 164.5–166°, lit.,[12,13] m.p. 166–167°; neut. equiv., calcd. 71.4, found, 71.8.

Anal. Calcd. for $C_9H_{14}O_6$: C, 49.54; H, 6.47. Found: C, 49.54; H, 6.25.

Reaction of α-pinene oxide with glacial acetic acid.[25] Pinene oxide, 3 g., was added to 20 cc. of glacial acetic acid and the solution was heated on the steam bath for 2 hr. Workup of the crude reaction product[5] gave an aldehyde fraction. The semicarbazone formed from this fraction melted at 137–139° after recrystallization twice from ethyl acetate–ligroin solvent.

Gas chromatographic analysis of this aldehyde fraction indicated the presence of III and IV in the ratio 3:17.

Acknowledgment. We wish to thank the Stauffer Chemical Company and the Allied Chemical Corporation for Fellowship Grants.

EVANSTON, ILL.

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(25) According to the method of Royals, Ref. 5, or Arbuzov, Ref. 3.