[Contribution from the Research Department, The Givaudan Corp.]

Structural Studies in the Citronellyl and Rhodinyl Series. The Synthesis of Rhodinal and Rhodinol

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Received February 27, 1961

The synthesis of pure rhodinal by the dehydration of hydroxycitronellal has been achieved. Both rhodinal and citronellal were reduced by the Wolff-Kishner method to 2,6-dimethyl-1-octene and 2,6-dimethyl-2-octene, respectively. The ozonolysis of the olefin from rhodinal afforded 6-methyl-2-octanone, that from citronellal, 4-methylhexanal. The ozonolysis of rhodinol yielded 6-methyl-8-hydroxy-2-octanone whereas ozonolysis of citronellol resulted in a complex mixture of cyclic epoxy derivatives of 4-methyl-6-hydroxyhexanal.

The early work of Barbier and Locquin[1] reporting the formation of rhodinol, an isomer of citronellol with a more marked rose odor, by means of the sulfuric acid dehydration of hydroxycitronellol started the old and well publicized controversy on the citronellol-rhodinol structures[2] which cast doubt even on the reliability and value of ozonization as a tool for the determination of their structure.[2,3]

The dehydration of hydroxycitronellal first reported by Verley[2] to favor the formation of rhodinal has been carried out under a variety of conditions by later workers.[4] However, the reported constants of the rhodinal preparations gave no conclusive evidence of purity; in particular, the melting points and mixed melting points of the semicarbazones of the rhodinal preparations with that of pure citronellal failed to confirm the presence of pure preparations with the α-isopropenyl form exclusively.

Additional work was done to study the citronellyl-rhodinyl structure of terpenes and related compounds by Naves[5] using Raman spectra and infrared spectroscopy; the spectroscopic data became indeed a powerful tool in the detection of both the α-isopropenyl and the β-isopropylidene forms which until then were determined from the ozonolysis[6] fragments, formaldehyde and acetone. Because of the ease of cyclization of citronellal[7] to isopulegol some of the formaldehyde was derived from the isopropenyl structure of isopulegol. Hence, ozonolysis of citronellal always led to high values for the α- form.

The preparation of essentially pure samples of rhodinal and citronellal as well as the ozonolysis of stable and reliable derivatives of these products was the aim of our present work. As a result of this we have established that both rhodinol with the α or isopropenyl structure and citronellol with the β- or isopropylidene structure are capable of existing in pure and individual states and the assumption that the alcohols as well as their corresponding aldehydes were identical or existed in an unseparable mixture of the two forms[8] has lost its substance.

Dehydration of hydroxycitronellal over alumina at 350° afforded a mixture consisting of about 75% rhodinal and 25% of an equal mixture of citronellal and isopulegol. An attempt to isolate rhodinal from this mixture by the bisulfite method described by Verley[2] in his preparation of rhodinal failed and only the small amount of citronellal present was recovered. This confirmed indeed Verley's statement that rhodinal sulfonated very readily but, at the same time, strengthened the assumption of Grignard and Doeuvre[3] that the rhodinal and its semicarbazone, m.p. 75.5°, claimed by Verley consisted largely of racemized citronellal. On the other hand, it was found that, unlike citronellal, the rhodinal is particularly stable and practically unaffected by mild acid catalysts such as silica gel. Indeed, when a mixture of rhodinal and citronellal was distilled over silica gel around 125°, the rhodinal was recovered unchanged whereas practically all the citronellal was converted into isopulegols. It is possible then to conclude that the mechanism of cyclization to isopulegol (IV), unlike the one suggested by Semmler,[9] requires the isopropylidene structure of citronellal (I) which facilitates the cyclization of its conjugate acid II into the isopulegol carbonium ion III. In the case of rhodinal (V) the conjugate acid VI does not have the proper electron density in the carbon involving the cyclohexane ring and the cyclization fails to materialize.

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[1] P. Barbier and R. Locquin, *Compt. rend., acad. sci.*, **157**, 1114 (1913).

[2] A. Verley, *Bull. soc. chim. France* [4], **43**, 845, 854 (1928).

[3] V. Grignard and J. Doeuvre, *Bull. soc. chim. France* [4], **45**, 809 (1929).

[4] M. F. Carroll, R. G. Mason, H. W. Thompson, and R. C. S. Wood, *J. Chem. Soc.*, 3457 (1950). R. L. Webb, U.S. Patent **2,902,495** (1959).

[5] Y. R. Naves, G. Brus, and J. Allard, *Compt. rend acad. sci.*, **200**, 1112 (1935). Y. R Naves, *Bull. soc. chim. France*, 505 (1951).

[6] J. Doeuvre, *Bull. soc. chim. France* [5], **3**, 612 (1936).

[7] Even active carbon is reported to be an effective catalyst for cyclization, *cf.* S. Kimura, *Bull. Chem. Soc. Japan*, **10**, 330 (1935).

[8] J. L. Simonsen in *The Terpenes*, Vol. I, University Press, Cambridge, 1947, pp. 35, 37, 73, 74, 75, 80.

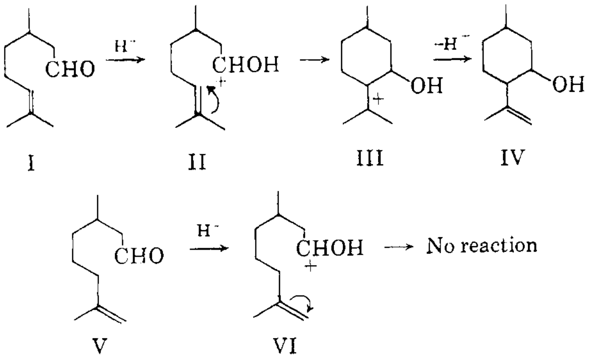
[9] F. W. Semmler, *Ber.*, **42**, 2016 (1909).

A shift of the double bond from the isopropenyl to the isopropylidene structure, as suggested by Simonsen,[8] would probably not take place in the case of rhodinal unless drastic acidic conditions were used, and then the self-condensation of the rhodinal would compete to a great extent with its possible conversion into isopulegols.

Boration of the rhodinal-isopulegols mixture afforded rhodinal in pure state. It is assumed therefore that the original dehydration product of hydroxycitronellal consists of about 75% rhodinal and 25% citronellal but because of the slight acidity of the alumina used half of the citronellal formed is converted into isopulegols.

Rhodinal and methanol reacted in the presence of *p*-toluenesulfonic acid to give an excellent yield of the dimethyl acetal.

Pure rhodinol was prepared by the lithium aluminum hydride reduction of rhodinal and showed constants close to those reported for a 95% pure α-citronellol isolated by Sutherland[10] from β-citronellol by repeated fractional distillation of a benzoyl chloride–treated citronellol. Rhodinyl acetate was also prepared by treating rhodinol with acetic anhydride.



Mixtures of citronellal, rhodinal, and isopulegols were analyzed[11] by gas-liquid chromatography using two different columns. Rhodinal was separated from either citronellal or isopulegols in an acidic Celatom FM 73 column. In either case only two peaks were obtained: one for rhodinal (6.6 min.) and the other for *trans*-isopulegol (9.5 min.); with a mixture of rhodinal and citronellal this column gave the same two peaks. But with a citronellal-isopulegol mixture only one peak (9.5 min.), corresponding to *trans*-isopulegol, resulted. The acidic Celatom FM-73 column therefore selectively cyclized citronellal to *trans*-isopulegol without affecting rhodinal.

Citronellal and isopulegols were separated with a neutral Chromosorb-W column which gave a peak corresponding to citronellal (6.6 min.) followed by two peaks (9.5 min. and 11.2 min.) for *trans*- and *cis*-isopulegol, respectively. This column, however, did not separate a mixture of citronellal and rhodinal and showed a single peak (6.6 min.) for both aldehydes.

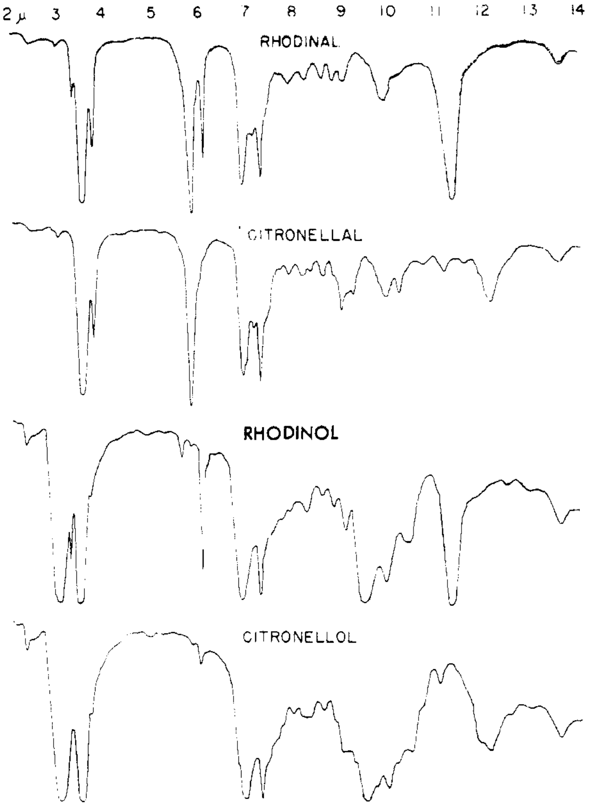


Fig. 1. Infrared spectra of rhodinal, citronellal, rhodinol and citronellol

Rhodinal was determined from the acidic Celatom FM-73 chromatogram, isopulegols from the Chromosorb-W chromatogram, whereas citronellal was calculated by difference between the combined rhodinal-citronellal value of the Chromosorb-W chromatogram and the rhodinal value of the Celatom FM-73 chromatogram.

The evaluation of rhodinal in mixtures with citronellal can also be made using the 6.1 μ infrared absorption band of rhodinal (Fig. 1). However, the presence of isopulegols interferes with this determination since it also shows the same absorption at 6.1 μ.

Pure citronellal from the Oil of Citronella Java was made essentially according to Grignard and Dœuvre[3] from its bisulfite compound; the constants of citronellal agreed closely with those reported. It afforded a semicarbazone, m.p. 84° and, like the citronellal reported in the later work of Dœuvre[12] it proved by infrared analysis and gas-liquid chromatography to be free of any rhodinal. The absence of rhodinal in the bisulfite purified citronellal is

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(10) M. D. Sutherland, *J. Am. Chem. Soc.*, **73,** 2385 (1951); **74,** 2668 (1952).

(11) We wish to express our thanks to Mr. P. Porcaro of our Analytical Department for his successful efforts in preparing the chromatographic columns, described in the experimental part which lead to the determination of rhodinal, citronellal, and isopulegols.

(12) J. Doeuvre, *Bull. soc. chim. France* [5] **3,** 615 (1936).

not surprising if we assume that any rhodinal originally present in the Oil of Citronella Java would remain in the aqueous phase as the sulfonate.

Both rhodinal and citronellal were reduced in excellent yields by the Wolff-Kishner method to the respective hydrocarbons. Citronellal afforded 2,6-dimethyl-2-octene[13]; rhodinal, on the other hand, gave 2,6-dimethyl-1-octene. With lithium aluminum hydride the aldehydes afforded citronellol and rhodinol, respectively.

Compound	B.P.	n_D^{20}	$[\alpha]_D^{25}$	Semi-carbazone	2,4-Dinitro phenyl-hydrazone
Citronellal	47° at 1 mm.	1.4460	+11.5°	84°[17]	81–82°[17]
Rhodinal	51° at 1.4 mm.	1.4410	9.75°	73°[17]	73–74°
Citronellol	84° at 1.8 mm.	1.4560	4.0°		
Rhodinol	79° at 1.7 mm.	1.4520	2.5°		
2,6-Dimethyl-2-octene	67° at 50 mm.	1.4300	7.0°		
2,6-Dimethyl-1-octene	163° at 745 mm.	1.4260	6.5°		
4-Methylhexanal	67° at 50 mm.	1.4148	6.5°	124°	91°
6-Methyl-2-octanone	100° at 50 mm.	1.4220	6.0°	132°	62°

The ozonolysis of 2,6-dimethyl-1-octene and 2,6-dimethyl-2-octene was carried out in the presence of aqueous acetic acid as participating solvent and resulted in an almost quantitative yield of the degradation products. Thus, 2,6-dimethyl-1-octene afforded 6-methyl-2-octanone, semicarbazone m.p. 132°; 2,4-dinitrophenylhydrazone m.p. 61°; whereas 2,6-dimethyl-2-octene yielded 4-methylhexanal, semicarbazone m.p. 124°; 2,4-dinitrophenylhydrazone m.p. 91°.

The ozonolysis of rhodinol in aqueous acetic acid or aqueous methanol solutions afforded 6-methyl-8-hydroxy-2-octanone, b.p. 115° at 1.5 mm. n_D^{20} 1.4998: $[\alpha]_D^{25}$ + 3°. The ozonolysis of citronellol in aqueous acetic acid afforded a product corresponding to 4-methyl-6-hydroxyhexanal: when freshly distilled the refractive index was around n_D^{20} 1.4500 but rose in twenty to thirty minutes to a constant value of about 1.4700.[14]

A study of the infrared spectrum of the freshly distilled product showed a significant decrease in absorbance of the (5.85 μ) aldehyde band during the short period of equilibration indicating formation of a hemiacetal, probably, 4-methyloxepan-2-ol. However, the sizes of the hydroxyl and carbonyl bands at equilibrium still indicate a substantial amount of the acyclic form as has been suggested by Hurd and Saunders.[15]

When the ozonolysis of citronellol was carried out in aqueous methanol solution and the ozonizate treated with zinc and sulfuric acid, a sizable amount of the reaction product consisted of the acetal, 2-methoxy-5-methyloxepane reported by Helfrich and Sparmberg,[14] together with a higher boiling product with an infrared spectrum similar to that of the product obtained from the ozonolysis in aqueous acetic acid solution. A mechanism for the cyclization of analogous hydroxyaldehydes has been suggested by Colonge and Corbet.[16]

The table above shows the physical constants of rhodinal and citronellal including their derivatives, as well as their degradation products.

EXPERIMENTAL

Citronellal. One thousand g. of crude bisulfite-citronellal compound, from the bisulfitation of 80% citronellal, obtained by distillation from oil of the citronella Java, and washed with a hydrocarbon solvent (xylene, benzene, or hexane) was kneaded with 1500 ml. of the same solvent and the slurry filtered over a large suction funnel. The cake was then washed with an additional 1000 ml. of solvent until the filtrate was free from residual oil. The dried bisulfite compound was then added, with stirring at 80°, to a solution of 600 g. of sodium carbonate in 3 l. of water.

Crude citronellal (335 g.), n_D^{20} 1.4462 was obtained showing a purity of 97.6% by oximation. A further extraction with three 300-ml. portions of benzene yielded an additional amount (12 g.) of citronellal. Upon distillation over a 100-cm. stainless steel Cannon-packed column the main bulk of the citronellal distilled at 47° under 1 mm. pressure, n_D^{20} 1.4460; $[\alpha]_D^{25}$ + 11.50° aldehyde by oximation 100%. The semicarbazone, after four recrystallizations from hexane, showed a m.p. of 84°.

Anal. Calcd. for $C_{11}H_{21}N_3O$: C, 62.51; H, 10.02; N, 19.88. Found: C, 62.29; H, 9.86; N, 19.69.

2,4-Dinitrophenylhydrazone, yellow plates, m.p. 81–82° (ethanol).

Anal. Calcd. for $C_{16}H_{22}N_4O_4$: C, 57.48; H, 6.63; N, 16.76. Found: C, 57.38; H, 6.54; N, 16.62.

Rhodinal. Hydroxycitronellal (830 g.) (Laurine® Givaudan) n_D^{20} 1.4480, $[\alpha]_D^{25}$ + 9.75°, was introduced at a rate of 100 ml. per hour at 350° into a borosilicate glass column, 100 cm. long and 25 mm. in diameter, containing 200 g. of

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[13] L. Wolff, *Ann.*, **394**, 86 (1912), reported formation of 2,6-dimethyl-2-octene without proof of structure.

[14] B. Helfrich and G. Sparmberg, *Ber.*, **64**, 104 (1931), reported a hydroxyaldehyde derived from the ozonization of citronellyl acetate; the constants of which would correspond to those of the equilibrium mixture.

[15] C. D. Hurd and W. H. Saunders, *J. Am. Chem. Soc.*, **74**, 5324 (1952).

[16] J. Colonge and P. Corbet, *Bull. soc. chim. France*, 283, 287 (1960).

[17] C. F. H. Allen, *J. Am. Chem. Soc.*, **52**, 2955 (1930), reports an m.p. of 78° for citronellal 2,4-dinitrophenylhydrazone. Y. R. Naves, L. Desalbres, and P. Ardizio, *Bull. soc. chim. France*, 1772 (1956), report an m.p. of 79–80° for optically active citronellal 2,4-dinitrophenylhydrazone and an m.p. of 89–90° for the racemic derivative. The semicarbazone of the racemic citronellal is reported to melt at 82–82.5°. Caroll and co-workers[4] report a m.p. of 85° for semicarbazone of citronellal and an m.p. of 65° for that of rhodinal.

$^1/_4$ to 6 in. mesh activated alumina (grade F-1, Aluminum Co. of America). The reaction product (758 g. n_D^{20} 1.4485) was separated from the water (71 ml.) and distilled. Crude rhodinal 528 g.; n_D^{20} 1.4480; b.p. 55–60° at 0.5 mm. pressure was collected. It showed by analysis[11] 75% rhodinal, 12% citronellal, and 13% isopulegol. The residue of 210 g. consisted mainly of unreacted hydroxycitronellal good for recyclization.

The crude distilled rhodinal (528 g.) containing a total of about 25% citronellal-isopulegol mixture was mixed with 16 g. of boric anhydride, 5 g. of silica gel, and 300 ml. of toluene and refluxed at 130–135° with a Dean-Stark trap. After about 1 hr. no more water (*ca.* 8 ml.) was formed and the solvent was evaporated. The pure rhodinal was then distilled from the residual isopulegol borate in a 95% yield, b.p. 51° at 1.4 mm. n_D^{20} 1.4410; $[\alpha]_D^{25}$ + 9.75°. It showed a rhodinal content of over 99% with only traces of isopulegol and citronellal present. The semicarbazone showed an m.p. of 73° from ethanol.

Anal. Calcd. for $C_{11}H_{21}N_3O$: C, 62.51; H, 10.02; N, 19.88. Found: C, 62.62; H, 10.08; N, 20.10.

2,4-Dinitrophenylhydrazone, m.p. 73–74°, from ethanol.

Anal. Calcd. for $C_{16}H_{22}N_4O_4$: C, 57.48; H, 6.63; N, 16.76. Found: C, 57.48; H, 6.49; N, 16.98.

d-Citronellol. Pure *d*-citronellal (103 g.), n_D^{20} 1.4460, $[\alpha]_D^{25}$ + 11.50° in dry ether (50 ml.) was added to a solution of lithium aluminum hydride (8 g.) in dry ether (250 ml.) within 15 min. The reaction mixture was refluxed for 1 hr. and then decomposed with 5 ml. of ethyl acetate followed by 100 ml. of water. The slurry was then carefully acidified with dilute sulfuric acid, washed with water, and neutralized. After evaporation of the solvent the citronellol was carefully distilled in a 100-cm. Cannon-packed (Ni) column and the main cut (70 g.), collected at 84–85° at 1.8 mm. pressure, n_D^{20} 1.4560; $[\alpha]_D$ + 4°.

An identical citronellol was obtained in the Meerwein-Pondorf reduction using 154 g. of citronellal, 75 g. of aluminum isopropylate and 500 ml. of dry isopropyl alcohol. After 4 hr. of refluxing acetone (*ca.* 70 ml.) was collected; then isopropyl alcohol (300 ml.) was distilled and the residue worked out with aqueous acetic acid. After distillation, a main cut of 120 g. of *d*-citronellol, b.p. 72° at 1 mm. pressure, n_D^{20} 1.4560; $[\alpha]_D^{25}$ + 4° was obtained; the infrared absorption curve showed no bands at 6.1 or 11.3 μ.

Rhodinol. Rhodinal (103 g.) n_D^{20} 1.4410; $[\alpha]_D$ + 9.75° in 100 ml. of dry ether was treated with lithium aluminum hydride (7.3 g.) in 200 ml. of dry ether. The reaction procedure was essentially similar to that used in the preparation of citronellol. The main bulk of rhodinol (70 g.) distilled at 79° at 1.7 mm. pressure, n_D^{20} 1.4520, $[\alpha]_D$ + 2.5°. Infrared spectrum with strong methylenic ($C{=}CH_2$) absorption bands at 6.1 and 11.3 μ.

2,6-Dimethyl-2-octene. Citronellal (46.5 g.) n_D^{20} 1.4460, $[\alpha]_D$ + 11.5°, 300 ml. of diethyleneglycol, 30 ml. of 85% hydrazine hydrate, and 52 g. of potassium hydroxide pellets were refluxed at 140° for 30 min.; the glycol was then distilled until the reaction temperature reached 180°. The distillate was shaken with a saturated solution of sodium chloride and the top layer of hydrocarbon (*ca.* 30 g.) returned to the reaction flask and refluxed for 3 hr. at 180°. The reaction mixture was then distilled until the pot temperature reached 250°. The distillate was again treated with saturated sodium chloride solution and the top layer separated and washed with a 10% sulfuric acid solution. After neutralization and distillation over sodium, the 2,6-dimethyl-2-octene (34 g., 80%) distilled at 67° at 26 mm. pressure, n_D^{20} 1.4300, $[\alpha]_D$ + 7°; it showed no characteristic methylenic ($C{=}CH_2$) bands at 6.1 and 11.3 μ in the infrared region of the spectrum.

2,6-Dimethyl-1-octene. Thirty ml. of 85% hydrazine hydrate was added to 46.5 g. of rhodinal, n_D^{20} 1.4410, $[\alpha]_D$ + 9.75° in 300 ml. of diethylene glycol. The temperature of the reaction mixture rose to about 50°; then 52 g. of potassium hydroxide pellets was added and the reaction mixture refluxed for 30 min. Diethylene glycol was distilled until the reaction temperature reached 180°. The distillate was washed with saturated sodium chloride solution and the top layer returned to the reaction vessel and the refluxing was resumed for an additional 3 hr. The reaction mixture was finally distilled until the pot temperature reached 250°. The distillate was treated with saturated sodium chloride solution, washed with 10% sulfuric acid, neutralized, and finally distilled over sodium. A 38.5-g. quantity of product (88%) was obtained which distilled at 163° at 745 mm. pressure, n_D^{20} 1.4260, $[\alpha]_D^{25}$ + 6.5°. The product showed the characteristic terminal methylenic ($C{=}CH_2$) absorption bands at 6.1 and 11.3 μ in the infrared region of the spectrum.

4-Methylhexanal. A mixture of 19 g. of 2,6-dimethyl-2-octene, n_D 1.4300, $[\alpha]_D$ + 7° and 57 ml. of 66% aqueous acetic acid was ozonized at 0° with a stream of ozonized oxygen (*ca.* 60 mg. of ozone/oxygen) at a rate of 33 l. per hr. using a model T 23 Welsbach ozonator. After about 2 hr. the reaction mixture became homogeneous and the ozone started to escape free from the reaction vessel. The ozonizate was then added to an agitated mixture of 10 g. of powdered zinc in 150 ml. of water; the temperature rose to 70° within 5 min. and the stirring was continued for an additional hour under a nitrogen atmosphere until the temperature fell to about 30°. The oily layer was separated and the mother liquors were extracted with ether; after neutralization with sodium bicarbonate and evaporation of the solvent, 14 g. of 4-methylhexanal (91%) was obtained which distilled at 67° at 50 mm., n_D^{20} 1.4148, $[\alpha]_D^{25}$ + 6.5°. Semicarbazone, m.p. 124° (benzene).

Anal. Calcd. for $C_8H_{17}N_3O$: C, 56.11; H, 10.01; N, 24.54. Found: C, 56.33; H, 9.92; N, 24.61.

2,4-Dinitrophenylhydrazone, m.p. 91° (ethanol).

Anal. Calcd. for $C_{13}H_{18}N_4O_4$: C, 53.05; H, 6.16; N, 19.03. Found: C, 53.26; H, 6.42; N, 18.93.

6-Methyl-2-octanone. A mixture of 19.5 g. of 2,6-dimethyl-1-octene, n_D^{20} 1.4260; $[\alpha]_D^{25}$ + 6.5°; in 60 ml. of 66% aqueous acetic acid was ozonized under the same conditions described in the previous experiment for 2,6-dimethyl-2-octene. The ozonizate was then decomposed with 10 g. of powdered zinc in 150 ml. of water, and 17 g. of 6-methyl-2-octanone (100%) was obtained which distilled at 100° at 50 mm., n_D^{20} 1.4220; $[\alpha]_D^{25}$ + 6°. Semicarbazone, m.p. 132° (benzene).

Anal. Calcd. for $C_{10}H_{21}N_3O$: C, 60.26; H, 10.62; N, 21.08. Found: C, 60.34; H, 10.71; N, 21.14.

2,4-Dinitrophenylhydrazone, m.p. 62° (ethanol).

Anal. Calcd. for $C_{15}H_{22}N_4O_4$: C, 55.88; H, 6.88; N, 17.38. Found: C, 56.14; H, 6.98; N, 17.48.

Ozonolysis of rhodinol. A mixture of 15.5 g. of rhodinol, n_D^{20} 1.4520 $[\alpha]_D$ + 2.5° and 46.5 ml. of 66% aqueous acetic acid was ozonized at 0° according to the technique described in the previous experiment. Decomposition of the ozonizate with 10 g. of powdered zinc and 150 ml. of water afforded 6-methyl-8-hydroxy-2-octanone (93%), b.p. 115° at 1.5 mm., n_D^{20} 1.4498, $[\alpha]_D$ + 3°.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.30; H, 11.46. Found: C, 68.20; H, 11.26.

The same results were obtained when the ozonization of rhodinol (15.5 g.) was carried out in 66% methanol solution (46.5 ml.) and the decomposition of the ozonizate made at 50° in water (100 ml.), zinc (10 g.) and 50% sulfuric acid (50 ml.).

Ozonolysis of citronellol. (a) *With aqueous acetic acid.* A mixture of 31 g. of citronellol n_D^{20} 1.4560, $[\alpha]_D$ + 4° in 93 ml. of 66% aqueous acetic acid was ozonized under the same conditions described for the ozonolysis of rhodinol. After decomposition of the ozonizate with 20 g. of powdered zinc in 200 ml. of water for 30 min. at 50–55°, the clear solution obtained was decanted from the unchanged zinc, saturated with sodium chloride, and extracted with ether. The ether extract was washed with water, neutralized bicarbonate solution, and evaporated. The residue was distilled in a short Claisen-Vigreux flask as follows:

Cut 1: b.p. 70–72 at 1.2 mm. pressure 4 g., n_D^{20} 1.4705 (after 24 hr.); $[\alpha]_D^{25}$ + 16°.

Cut 2: b.p. 74–78° at 1.2 mm. pressure, 15 g., n_D 1.4720 (after 24 hr.); $[\alpha]_D^{25}$ + 19°.

Residue: 1 g.

The refractive index of the freshly distilled product varied with the time until it reached a constant reading after about 1 hr.:

Time	Cut #1	Cut #2
1 min.	1.4555	1.4520
5 min.	1.4650	1.4580
10 min.	1.4660	1.4610
90 min.	1.4705	1.4712
24 hr.	1.4705	1.4720

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.6; H, 10.84. Found: C, 64.25; H, 10.68.

The infrared spectra of freshly distilled cuts (1–5 min.) looked very similar; they exhibited strong absorption bands at the hydroxyl (3.1 μ), carbonyl (5.85 μ), and alkoxy (wide 9–10 μ) bands. Older samples (1–24 hr.) showed the same characteristic bands but with a considerable regression of the carbonyl band (5.85 μ) and appearance of a band at 10.8 and 11.2 μ.

(b) *Ozonolysis in aqueous methanol.* A mixture of 31 g. of citronellol in 46.5 ml. of 60% aqueous methanol was ozonized as described in (a); the clear ozonizate was introduced at room temperature into a mixture of 20 g. of powdered zinc and 200 ml. of water and stirred for 5 min.; no rise in temperature occurred as no reaction seemed to take place. Then 100 ml. of 50% sulfuric acid was introduced within 5 min. while the temperature rose to 75°. Stirring was continued for 5 more min. and the temperature began to fall to 65°. The clear solution was then decanted from the unchanged zinc, saturated with sodium chloride and extracted with ether; after washing with a saturated solution of sodium chloride, the ether extract was neutralized with sodium bicarbonate and the solvent evaporated to yield a crude residue of about 25 g. Upon distillation in a short Vigreux flask the following cuts were obtained:

Cut 1: b.p. 65–67° at 28 mm., 9 g.; n_D^{20} 1.4350, $[\alpha]_D^{25}$ + 97°.

Cut 2: b.p. 80–93° at 1.5 mm., 6 g.; n_D^{20} 1.4467 (5 min.), 1.4592 (24 hr.), $[\alpha]_D$ + 14°.

Cut 3: b.p. 100–120° at 1.5 mm. 4 g.; n_D 1.4562 (5 min.), 1.4600 (24 hr.), $[\alpha]_D$ + 42°

Residue: 3 g.

Cut 1.

Anal. Calcd. for 2-methoxy-5-methyloxepane ($C_8H_{16}O_2$): C, 66.6; H, 11.19. Found C, 66.36; H, 10.62.

Rhodinal dimethyl acetal. Rhodinal (105 g.) and methanol (170 g.) were mixed at room temperature under stirring and after the initial rise of temperature (about 10°) subsided, 0.2 g. of *p*-toluenesulfonic acid was added and the mixture was agitated for 4 hr. at 35°. The reaction mixture was made alkaline to phenolphthalein with aqueous sodium hydroxide and the excess methanol evaporated under coarse vacuum (50 mm. pressure). The main bulk of the acetal (108 g.) distilled at 64° at 0.8 mm. pressure, n_D^{20} 1.4352, $[\alpha]_D$ + 3.75°.

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.98; H, 12.08. Found: C, 72.09; H, 12.16.

Rhodinyl acetate. A mixture of rhodinol (50 g.), acetic anhydride (75 g.) and sodium acetate (10 g.) was refluxed around 140° for 3 hr.; after cooling at 60° 200 ml. of water was added and the mixture agitated for 10 min. to decompose the excess anhydride. The crude acetate was then separated, neutralized with aqueous sodium carbonate, and distilled. The main portion of the ester (54 g.) distilled at 75° at 1 mm. pressure, n_D^{20} 1.4388, $[\alpha]_D^{25}$ + 2.5°.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.69; H, 11.18. Found: C, 72.82; H, 11.07.

Analytical procedures.[11] Gas-liquid chromatograms were obtained with a Perkin-Elmer Vapor Fractometer, model 154 D, which was equipped with 8000 ohm thermistor detectors and a Leeds and Northrup 0–1 mv. recorder.

Column Substrate. Carbowax 20 M, polyethylene glycol compound, average mol. wt. 20,000 from Union Carbide Chemicals Co.

Column Supports. FM-73, a diatomaceous earth obtained from sweet water beds. It was used as supplied, *i.e.*, 48-65 mesh with no washing, from F&M Scientific Corp., New Castle, Del.

Chromosorb-W, a product of Johns-Manville similar to the familiar Celite-545. A 30- to 60-mesh material was acid washed (15% hydrochloric acid), freed from fines by decantation, and neutralized with dilute sodium hydroxide to *p*H 7.5. It was dried at 110° and finally screened to 30–60 mesh.

Prepared columns. Neutral Chromosorb-W. 30% Carbowax 20*M* on Chromosorb-W; 2 meters in length.

Acid Celatom FM-73. 30% Carbowax 20*M* on FM-73, 3 meters in length.

Column preparation. In each case Carbowax 20*M* and acetone were slurried with the solid support. The acetone was evaporated under thorough stirring and the final traces of solvent eliminated in a drying oven. The column material was then sieved and a 40- to 80-mesh crop collected. This was packed into 1/4″ O.D. copper tubing. Glass wool was used to plug each end. The column was subsequently coiled and fitted to the detector. Before connecting to the fractometer it was conditioned for 3 hr. at 225° with a slow stream of helium.

Instrument parameters.

	Neutral Chromosorb-W	Acidic Celatom, FM-73
Temperature	204°	219°
Pressure	15 p.s.i.	20 p.s.i.
Flow rate	31 ml./min. inlet; 43 ml./min. outlet	32 ml./min. inlet; 52 ml./min. outlet
Air peak elution	0.7 min.	0.9 min.
Sample size	0.4–0.6 μl	0.5–0.8 μl.
Attenuator	4	2
Bridge voltage	8	8
Chart speed	0.5 in./min.	0.5 in./min.

The two columns were checked under comparable conditions with 1:1 mixtures of citronellal-rhodinal, and citronellal-isopulegols.

The infrared absorption spectra of rhodinal, citronellal, and their corresponding alcohols (shown in Fig. 1) were run in a Perkin-Elmer instrument Model 21 with a sodium chloride prism and 0.025 mm. cell.

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