figurational assignments for the carveols are correct, and that the reassignments suggested by Farges and Kergomard[12] are invalid.

### Experimental

Melting points were taken in capillaries on a Mel-Temp melting point apparatus and are uncorrected. Boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 21 recording spectrophotometer. Gas–liquid chromatography separations were effected on a Wilkins Aerograph Master Model A-100 equipped with a 10-ft., 0.25-in., Carbowax 20 M column. Analyses were by G. Weiler and F. B. Strauss, Oxford, England.

**Reaction of *dl*-$\alpha$-Pinene Oxide with a Sodium Acetate–Glacial Acetic Acid Solution.**—Freshly distilled *dl*-$\alpha$-pinene oxide (136 g.), b.p. 63–65° (10 mm.), $n^{25}D$ 1.4670, was slowly added to a slurry of sodium acetate (123 g.) in glacial acetic acid (600 g.) over a period of 2.5 hr. The reaction temperature rose to approximately 40°. The reaction was stirred for 72 hr., during which time the temperature dropped to 27°. The reaction mixture was poured into 1000 ml. of water, the oil layer separated, and the aqueous phase extracted with three 100-ml. portions of ether. The organic phases were combined, neutralized with a saturated sodium bicarbonate solution, and washed with three 75-ml. portions of water. The ethereal phase was dried over anhydrous sodium sulfate. The ether was removed under reduced pressure and the product distilled over a 3-ft. spinning band column to give three fractions. The first fraction (53 g.) was campholenaldehyde (39%), b.p. 80° (10 mm.), $n^{25}D$ 1.4630, which gave a yellow 2,4-DNP, m.p. 110–111°, and semicarbazone, m.p. 138.5–140° (lit.[3] m.p. 139.5–140.5°).

*Anal.* Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.61; H, 10.63.

The second component (26 g.), b.p. 76° (4 mm.), $n^{25}D$ 1.4949, was identified as *dl-trans*-carveol (19.1%) by g.l.c. and infrared comparison with an authentic sample of *d-trans*-carveol. This alcohol formed a 3,5-dinitrobenzoate, m.p. 118–118.5° (lit.[13] $n^{19}D$ 1.4956, 3,5-dinitrobenzoate m.p. 119°).

*Anal.* Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.48; H, 10.55.

The third component (43.5 g.), b.p. 128–133° (4 mm.), $n^{25}D$ 1.4813, was subsequently identified as the monoacetate of sobrerol (*dl-trans*-8-acetoxy-6-hydroxy-1-*p*-menthene, 22.9%), which gave a 3,5-dinitrobenzoate, m.p. 130.5–132°.

*Anal.* Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.24; H, 9.72.

Saponification of the hydroxyacetate (0.4 g.) with a solution of 4 ml. of 50% potassium hydroxide in 10 ml. of a 20% ethanol solution afforded *dl-trans*-sobrerol, m.p. 128–129°, whose melting point was undepressed on admixture with an authentic sample.[6]

**Pyrolysis of *dl-trans*-8-Acetoxy-6-hydroxy-1-*p*-menthene.**—The sobrerol monoacetate (6.0 g.), produced above, was pyrolyzed at 370°. The pyrolysis product was taken up in ether, neutralized with a sodium bicarbonate solution, washed with water, and dried over anhydrous sodium sulfate. After removal of the solvent, the crude product (4.24 g.), identified by g.l.c. to be greater than 90% *trans*-carveol, was distilled on a modified Hickman still to give *dl-trans*-carveol (3.78 g.), $n^{25}D$ 1.4959, 3,5-dinitrobenzoate m.p. 119°. This alcohol gave an infrared spectrum identical with an authentic sample.

(12) G. Farges and A. Kergomard, *Bull. soc. chim. France*, 51 (1963).
(13) E. Guenther and D. Althausen, "The Essential Oils," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 203.

## An Improved Synthesis of Peroxybenzoic Acid

J. R. MOYER AND N. C. MANLEY

*The Dow Chemical Company, Midland, Michigan*

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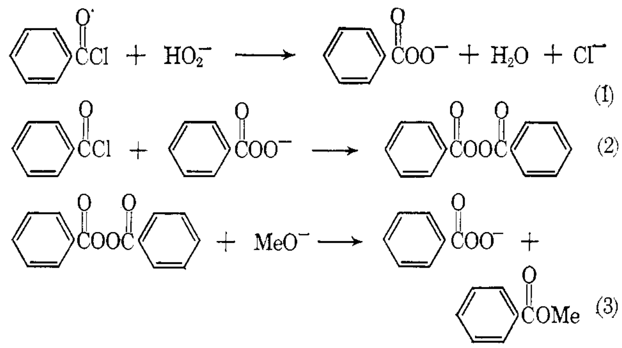
Peroxybenzoic acid is commonly prepared by a two-step process. In the first step, benzoyl chloride reacts with aqueous sodium peroxide. Because benzoyl chloride is immiscible with the solution, the reaction with the hydroperoxide ion (eq. 1) takes place at the surface of the droplets. The peroxybenzoate anion is less reactive toward benzoyl chloride than is $HO_2^-$, but reacts preferentially (eq. 2) because it is in contact. Several experimental procedures have been given.[1–3]

In the second step, benzoyl peroxide is cleaved by sodium methoxide (eq. 3). The procedure described by Braun[4] has been modified by later workers.[5,6]



Kergomard and Bigou[7,8] and Vilkas[9] have reported a method which avoids the formation of benzoyl peroxide. Sodium peroxide, or equivalent amounts of hydrogen peroxide and sodium hydroxide, is dissolved in a mixed solvent system in which benzoyl chloride is also soluble. In such a system, the peroxybenzoate ion and the hydroperoxide ion can compete as nucleophiles for benzoyl chloride. Very little benzoyl peroxide is formed. Peroxybenzoic acid can be recovered from the reaction mixture as soon as the addition of benzoyl chloride is complete.

This method is quicker, gives better yields, and is much safer in that neither benzoyl peroxide nor sodium metal is involved. It has the disadvantage of requiring a reaction temperature of −5° or lower.

We have had occasion to repeat many times this last method. We consistently obtain better yields using sodium peroxide rather than hydrogen peroxide and sodium hydroxide. Purification of the sodium peroxide by recrystallization as $Na_2O_2 \cdot 8H_2O$ gives further improvements in yield. This indicates that catalytic decomposition is occurring.

In commercial bleaching operations, the catalytic effect of traces of metal ions is inhibited by adding a small amount of magnesium sulfate.[10] We have found that the addition of a little magnesium sulfate to the reaction mixture allows the reaction to be run at room

(1) C. C. Price and E. Krebs, *Org. Syn.*, **23**, 65 (1943).
(2) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5432 (1950).
(3) J. D'Ans, J. Mattner, and W. Busse, *Angew. Chem.*, **65**, 57 (1953).
(4) G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 431.
(5) I. M. Kolthoff, T. S. Lee, and M. A. Mairs, *J. Polymer Sci.*, **2**, 199 (1947).
(6) C. G. Overberger and R. W. Cummins, *J. Am. Chem. Soc.*, **75**, 4250 (1953).
(7) A. Kergomard and J. Bigou, *Bull. soc. chim. France*, 486 (1956).
(8) A. Kergomard and J. Bigou, *ibid.*, 334 (1958).
(9) M. Vilkas, *ibid.*, 1501, (1959); French Patent 1,177,466 (1958).
(10) L. A. Beeman and J. S. Reichert, "The Bleaching of Pulp," R. S. Hatch, Ed., Technical Association of the Pulp and Paper Industry, New York, N. Y., 1953, p. 228.

temperature with yields equal to those obtained at −5° without the addition of magnesium sulfate.

### Experimental

A solution of 8.0 g. (0.102 mole) of sodium peroxide in 135 ml. of water is prepared with cooling so that the temperature does not exceed 20°. The solution is filtered through a "fine" porosity fritted disk to remove the yellow suspended solids. The filtrate is placed in a 1000-ml. beaker and stirred magnetically while 175 ml. of denatured ethanol and a solution of 0.5 g. of $MgSO_4 \cdot 7H_2O$ in 15 ml. of water are added. Heat liberated during the addition of ethanol raises the temperature of the solution about 8°.

When the solution is again at room temperature, 11.6 ml. (0.100 mole) of benzoyl chloride is added dropwise while the solution is stirred magnetically. The addition should take 10 to 12 min. The mixture is filtered to remove any benzoyl peroxide. The filtrate is acidified[11] with 20% sulfuric acid and extracted with carbon tetrachloride, chloroform, or benzene. Six extractions using about 75-ml. portions give 0.075 mole of peroxybenzoic acid. The entire procedure takes about 1.5 hr.

If ethanol is incompatible with subsequent reactants, methanol may be substituted. About 25 ml. of ethanol is extracted into the organic phase. Methanol is not extracted, but yields are about 60% *vs.* the 75% obtained using ethanol.

(11) Vilkas[9] reports better yields when the solution of sodium peroxybenzoate is added to the sulfuric acid rather than the converse.

## β-Ylangene, a New Sesquiterpene Hydrocarbon from Orange Oil

G. L. K. Hunter and W. B. Brogden, Jr.

*Fruit and Vegetable Products Laboratory, Southern Utilization Research and Development Division, Agricultural Research Service, Winter Haven, Florida*

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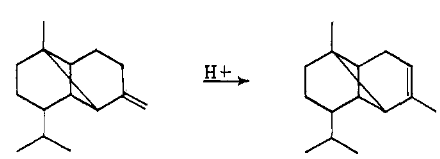
Previous work in this laboratory[1] showed that ylangene (I), hereafter called α-ylangene, was a stereoisomer of copaene. Copaene has recently been shown to contain a cyclobutane ring[2] in place of the cyclopropyl group which had previously been proposed.[3,4] In the present work the authors have isolated a new sesquiterpene hydrocarbon from Valencia orange oil which when reduced with $PtO_2$–$H_2$ at low pressure gave ylangane. This sesquiterpene hydrocarbon (II), hereafter called β-ylangene, therefore has the same stereochemistry as α-ylangene (I) and differs only in that it contains an exocyclic terminal double bond at position six instead of the endocyclic double bond at this position as is the case of α-ylangene. Isomerization of




II I

(1) G. L. K. Hunter and W. B. Brogden, Jr., *J. Org. Chem.*, **29**, 982 (1964).
(2) G. Büchi, S. H. Feairheller, P. DeMayo, and R. E. Williams, *Proc. Chem. Soc.*, 214 (1963); V. H. Kapadia, B. A. Nagasampagi, V. G. Naik, and Sukh Dev, *Tetrahedron Letters*, **No. 28**, 1933 (1963).
(3) L. H. Briggs and W. I. Taylor, *J. Chem. Soc.*, 1338 (1947).
(4) J. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, Cambridge University Press, London, 1952, p. 88.

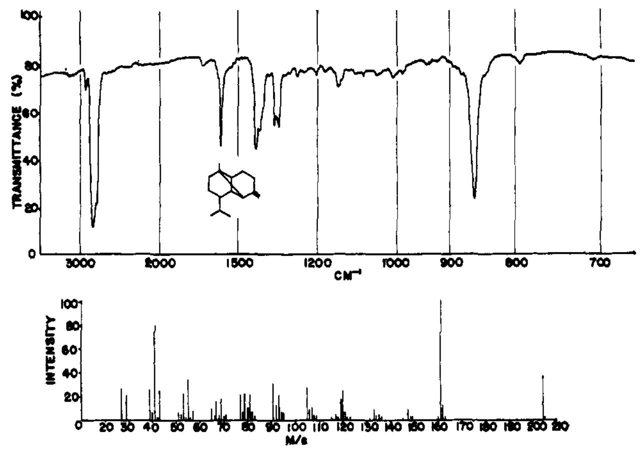



Fig. 1.—Infrared and mass spectra of β-ylangene.

β-ylangene in the presence of sulfuric acid gave α-ylangene.

### Experimental

**Isolation of β-Ylangene.**—Seven pounds of cold pressed Valencia orange oil was rapidly stripped of terpenes and low boiling oxygenated materials in an Arthur F. Smith 2-in. Rota-Film molecular still at 85° (1 mm.). The residue (200 g.) was redistilled in the same still, and 12 g. (0.3% of the total oil) boiling in the sesquiterpene range (100–110° at 0.25 mm.) was collected. The oxygenated compounds were removed from this fraction by elution with *n*-hexane through a 0.75 × 18 in. column containing basic alumina to give 1.7 g. (0.04% of the total oil) upon removal of the solvent *in vacuo*. This material was placed in a 0.75 × 36 in. column containing basic alumina and the first four fractions containing 3 ml. each were combined. Gas chromatographic[5] and infrared analyses of the residue upon removal of the solvent indicated the presence of α-copaene, α-ylangene, β-ylangene, and Δ-cadinene. The material having a retention time of 80 min., representing one of the major sesquiterpene constituents (0.008% of the total oil) was collected to give the infrared and mass spectra shown in Fig. 1. Absorptions at 1640 and 875 cm.$^{-1}$ showed the presence of a terminal double bond and those at 1387 and 1370 cm.$^{-1}$ indicated the presence of a *gem*-dimethyl group.[6] The principal peak at *m/e* 161 indicates the loss of the isopropyl fragment. β-Ylangene has a boiling point of 121–122° (10 mm.) by the method of Garcia[7] and a refractive index of $n^{20}D$ 1.5000.

**Reduction of β-Ylangene to Ylangane.**—Five microliters of β-ylangene was placed in a Parr apparatus with a catalytic amount of $PtO_2$ and allowed to shake for 4 hr. at room temperature under a hydrogen pressure of 70 lb./in.[2] to give a quantitative yield of ylangane. The infrared spectrum obtained on the material, following filtration of the catalyst, was identical in every respect with ylangane.[8] The molecular weight showed an increase of two in the *m/e* value by mass spectroscopy upon reduction of β-ylangene. The mass spectral cracking patterns after reduction of both β-ylangene and α-ylangene were identical.

**Isomerization of β-Ylangene to α-Ylangene.**—Five microliters of β-ylangene was placed in a vial containing a milliliter of 50% $H_2SO_4$ and shaken for 30 min. The emulsion was extracted with ether and gas chromatographed.[5] The material corresponding to the large peak, approximately 4 μl. of material and having the same retention time as α-ylangene, was collected. Infrared and mass spectra of this material were identical in all respects with the corresponding spectra of α-ylangene.[9]

(5) Column: 0.25-in. × 16-ft. containing 25% Carbowax 30M on Chromosorb P; flow rate, 60 ml./min.; temperature, programmed from 150–200° at 1.1°/min.
(6) N. Horak and J. Pliva, *Collection Czech. Chem. Commun.*, **25**, 1679 (1960).
(7) C. R. Garcia, *Ind. Eng. Chem. Anal. Ed.*, **15**, 648 (1943).
(8) J. Pliva, M. Horak, V. Herout, and F. Sorm in "Die Terpene. I. Sesquiterpene," Akademie, Verlag, Berlin, 1960, p. 220.
(9) Ref. 8, p. 221.