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.

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[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

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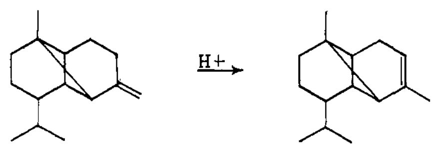
Previous work in this laboratory[1] showed that ylangene (I), hereafter called α-ylangene, was a stereoisomer of copaene. Copaene has recently been shown to contain a cyclobutane ring[2] in place of the cyclopropyl group which had previously been proposed.[3,4] In the present work the authors have isolated 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 β-ylangene in the presence of sulfuric acid gave α-ylangene.



II I

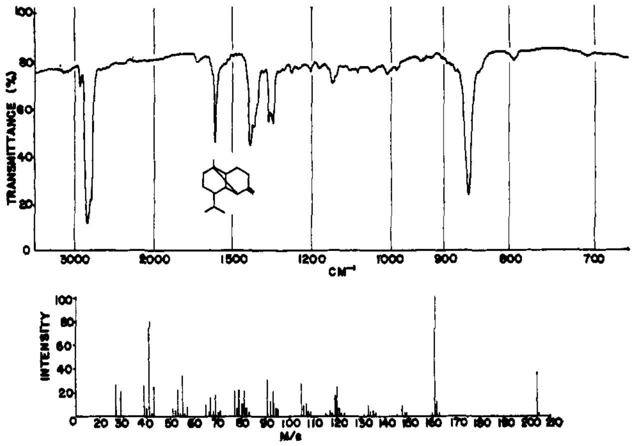


Fig. 1.—Infrared and mass spectra of β-ylangene.

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]

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[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.

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[9] Ref. 8, p. 221.