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A Chart of Ultraviolet Absorption Maxima of Semicarbazones

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A Colthup-type chart of the principal ultraviolet absorption maximum in the spectra in chloroform of several hundred 2,4-dinitrophenylhydrazones[1] suggested some possible utility in a similar analysis of the spectra of the other major carbonyl derivative, the semicarbazone. The source of data was again the three published volumes of "Organic Electronic Spectral Data"[2] supplemented by a rather unproductive search of *Chemical Abstracts* for 1960–1962. (Though many such spectra must have been published in those years, they appear to have been too widely scattered for indexing under general headings in Abstracts.)

A total of over 400 distinct semicarbazone spectra, nearly all of them in ethanol as solvent, were found. A frequency plot of the raw data for the entire group showed the largest numbers of entries in the 224–230- and 260–272-mμ regions, these corresponding to saturated and α,β-unsaturated carbonyl derivatives, respectively. In indexing the entries for the chart of Fig. 1 about 270 compounds were used, the remainder either lacking an identifiable structure or falling outside the classes of the index.

It is well-known that semicarbazone spectra are characterized by a moderately large bathochromic shift and an increase in molar absorptivity as compared to the parent carbonyl compounds.[3,4] A fairly regular increase in λ_{max} with the number of double bonds conjugated with the carbonyl and a corresponding rise in log ϵ also are noted generally.

As compared to either the carbonyl compounds or the 2,4-dinitrophenylhydrazones, however, the semicarbazones appear strikingly insensitive to most minor structural influences on their spectra. For example, aldehyde semicarbazones seldom differ enough from those of ketones to warrant separate chart entries, and the substitution of alkyl groups in α,β-unsaturated carbonyl compounds (*cf.* Woodward's rules) has an inappreciable effect on the semicarbazone spectra.

The only important structural effects are found in acetylcyclohexenes, methyl alkenyl ketones, and a few related compounds where the semicarbazones absorb at somewhat shorter wave lengths than other α,β-unsaturated systems (*cf.* Dorfman[5] for some explanatory notes on these), and in *o*-alkylacetophenones and a few highly alkylated cyclohexene derivatives where steric hindrance appears to account for decreased λ_{max} and log ϵ. An outstanding anomaly is the higher cycloalkenones whose semicarbazones absorb at 215 and 230 mμ,[6] well below the usual region for α,β-unsaturated compounds.

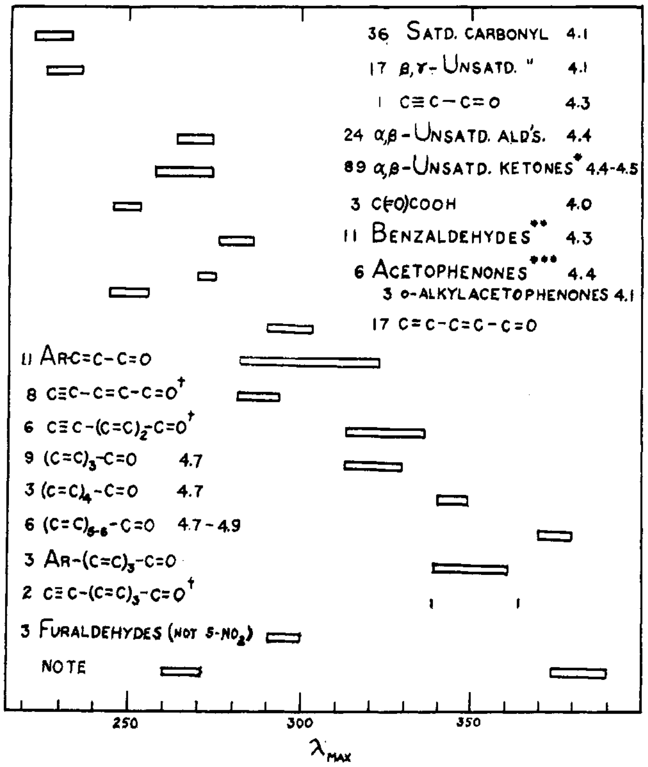

Fig. 1.—Principal maxima in the ultraviolet spectra of semicarbazones. Number of compounds in each class is given at left, and approximate log ϵ at right (when scatter of data is small); *, acetylcyclohexenes with λ_{max} near 260 mμ; **, salicylaldehyde falls below this indicated range for other benzaldehydes; ***, and higher homologs; $^+$, includes some compounds with triple bond position interchanged with one of the double bonds. (Note that this last group consists of ten 5-nitro-2-furylcarbonyl compounds, each having two maxima.)

For classification purposes in Fig. 1 compounds with isolated multiple bonds or other functions have all been grouped under the saturated carbonyl heading.

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Structure of Ylangene

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The structure of ylangene previously has not been proposed, although it had been isolated from many

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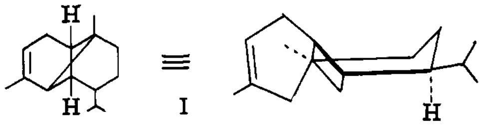
natural products.[2-5] Recently ylangene has been found by this laboratory to be a constituent of both grapefruit and orange essential oils. It also has been found to be one of the major sesquiterpenic constituents of cubeb oil.

Nuclear magnetic resonance spectra of ylangene and copaene were strikingly similar. Both spectra showed the presence of one vinyl proton, one vinyl methyl, one unsplit methyl, and two doublet methyls. The remaining protons were unresolved as the spectra were obtained using a microcell. This data and the molecular weight of 204 and 206 for ylangene and dihydroylangene (ylangane) by mass spectroscopy, respectively, indicated a tricyclic monoolefinic sesquiterpene hydrocarbon whose structure is similar to copaene, the latter obtained from cubeb oil according to Sŏrm.[6] Copaene recently has been shown by Büchi[7] to have structure I.



I

The infrared spectrum of ylangene was consistent with the copaene structure further demonstrating similarity absorbing at 790 and 780 $cm.^{-1}$, respectively, indicating a trisubstituted olefin. The mass spectrum cracking patterns of ylangene and copaene, shown in Fig. 1, differ only in minor details, strongly indicating identical structures. Reduction of ylangene and copaene with PtO_2/H_2 in the Paar apparatus resulted in the absorption of 1 mole of hydrogen by each, yielding ylangane and copane, respectively. The infrared spectra of these reduced sesquiterpenes were similar but not identical, and only minor differences were again noted between the mass spectra of these two compounds.

That ylangene and copaene are stereoisomers was shown by the reduction of both with Pd–carbon at 240° and 1550 p.s.i. of hydrogen, which is specific for the rupture of the cyclobutane ring according to Lukina,[8] to yield the single product cadinane. Attempts at reduction under less stringent conditions yielded only ylangane and copane, respectively. Furthermore, isomerization of both ylangene and copaene on silica gel at 100° for 30 min. yielded one major product and two minor products. The major product from both sources gave identical infrared spectra, and the three products from ylangene had the same retention times by gas chromatography and were in the same proportions as the analagous products from copaene. It is proposed that the mechanistic path followed by both ylangene and copaene during isomerization on silica gel is the same as that proposed for α-pinene[9] *i.e.*, attack on the allylic carbon with subsequent bond rupture between it and the tertiary carbon. This indicates that the cyclobutane ring has the same configuration in both sesquiterpenes. Assuming that the configuration at the isopropyl group remains the same and the difference lies at the ring junction centers, a structure (II) is proposed for ylangene. Manipulation of a Dreiding stereomodel of the probable cadinene precursor lends added support for the view.

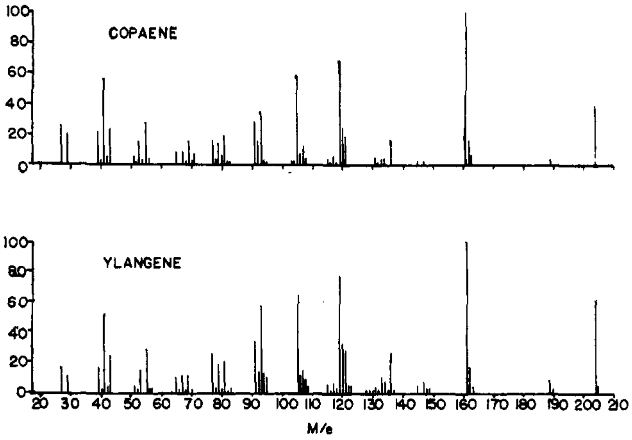
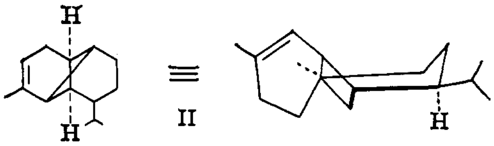


Fig. 1.—Mass spectral cracking pattern of copaene and ylangene.



II

Experimental

Reduction of Ylangene and Copaene.—Palladium-on-carbon catalyst was prepared according to the method of Brown and Brown.[10] Fifty microliters of ylangene and 10 mg. of catalyst were placed in an autoclave and heated to 240° under a hydrogen pressure of 1550 p.s.i. for 4.5 hr. A gas chromatograph having an 18 ft. × $^1/_4$ in. 25% Carbowax 20M on 30/60 Chromosorb-P column with a helium flow of 60 ml./min. and a column temperature of 160° yielded only one peak. The material represented by this peak was collected and shown to be identical with cadinane[11] by comparative infrared spectroscopy.

Copaene was treated in a manner described above for ylangene to yield identical results.

Isomerization of Ylangene and Copaene on Silica Gel.—Twenty microliters of ylangene were placed in a vial containing sufficient silica gel (Fisher Cat. No. S157) to form a slurry and heated at 100° for 30 min.

Acknowledgment.—The authors are indebted to Dr. Werner Herz for the n.m.r. studies.

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Ozonolysis of β-Brazan

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β-Brazan (I), or benzo[*b*]naphtho[2,3-*d*]furan, is known to be present in coal tar to a limited extent. Recently, this material has become available in ton quantities from Ruetgerswerke A. G. in Germany.[2]

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