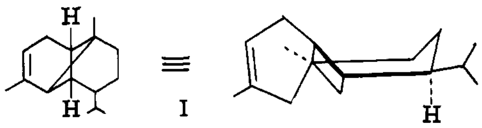
natural products.[2-5] Recently ylangene has been found by this laboratory to be a constituent of both grapefruit and orange essential oils. It also has been found to be one of the major sesquiterpenic constituents of cubeb oil.

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.

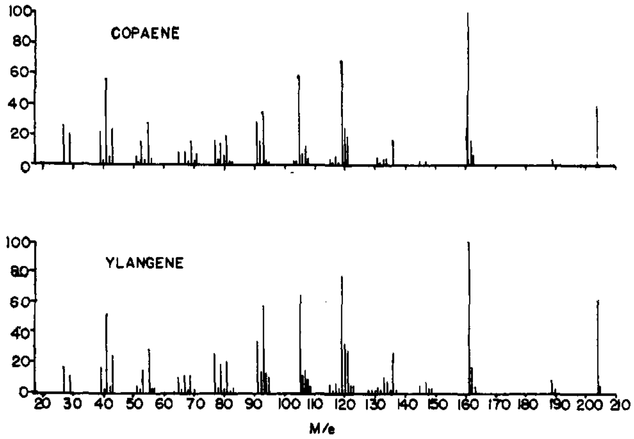
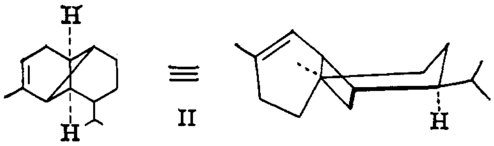


Fig. 1.—Mass spectral cracking pattern of copaene and ylangene.



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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(11) See ref. 6, p. S50.

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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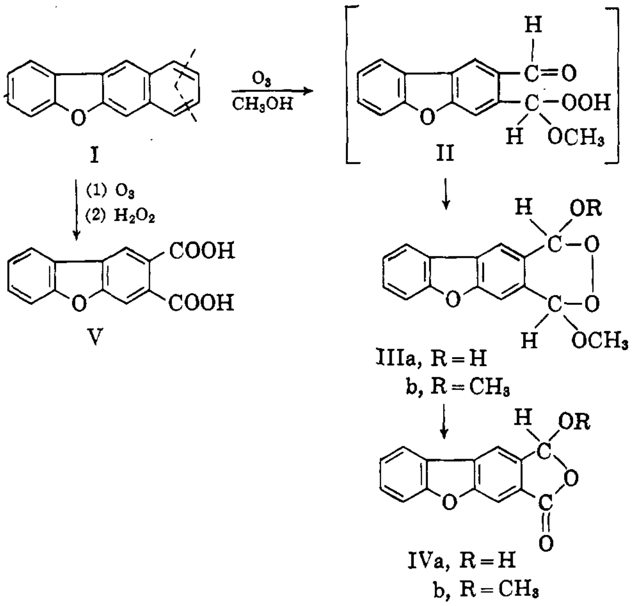
(2) Terra Chemicals, Inc., 500 Fifth Ave., New York 36, N. Y.

Previous work in this laboratory indicated that the parent compound, dibenzofuran, was resistant to attack by ozone.[3] It seemed of interest, therefore, to determine whether β-brazan would react with ozone. It was expected that the 7,8 and 9,10 bonds of β-brazan would be cleaved, ultimately yielding disubstituted derivatives of dibenzofuran. This was indeed found to be the case, and five compounds, not previously reported in the literature, have been isolated. Potentially, this offers a new route for the synthesis of certain difficultly accessible 2,3-disubstituted derivatives of dibenzofuran.

The ozonolysis was conducted in the protic solvent, methanol, to avoid the formation of ozonides or polymeric peroxides. Since I is virtually insoluble in methanol, a fine suspension was prepared by dissolving it in boiling carbon tetrachloride or methylene chloride followed by cooling and addition of methanol. Best results were obtained when the ozonolysis was conducted at about −25°. Approximately two molecular equivalents of ozone were absorbed before unchanged ozone escaped. The compounds which were isolated are those which would be predicted on the basis of the Criegee[4] mechanism for ozonolysis.

The probable course of the ozonolysis of I in methanol is shown below. Admittedly, such a scheme is an oversimplification. However, it does show in logical sequence the compounds that have been isolated. This reaction sequence is analogous to that which is known to occur during the ozonolysis of naphthalene in methanol,[5] although the yields of products are much lower and two different position isomers are possible with some of the compounds.



I

II

V

IIIa, R = H
b, R = CH₃

IVa, R = H
b, R = CH₃

(Where applicable, only one position isomer is shown.)

The experimental results lead to the following conclusions. At the end of the ozonolysis, the cold methanolic reaction mixture contains high concentrations of a methoxy hydroperoxide (II). This is evidenced by a strong lead tetraacetate test for hydroperoxide. With time and/or with an increase of temperature, the equilibrium shifts toward the more-stable and less-soluble cyclic tautomer (IIIa) which is a hemiperacetal. The best yield (34%) of crude hemiperacetal was obtained by evaporating the solvent mixture at reduced pressure, adding methanol, and filtering to collect the solids. The crude product was difficult to purify but appeared to be quite stable after purification. This hemiperacetal was assigned the structure of 1-(or 4-)hydroxy-4-(or -1-)methoxy-5,6-(2,3-dibenzofurano)-2,3-dioxane (IIIa) on the basis of its infrared spectrum and elemental analysis. However, it is not known whether this material is one isomer or a mixture of the two possible isomers.

An acid-catalyzed conversion of the hemiperacetal to a peracetal (IIIb) was effected by adding hydrogen chloride gas to the methanolic mixture and allowing it to stand at room temperature overnight. The best yield of peracetal obtained was 36%. This peracetal is very stable and could be purified by crystallization from tetrahydrofuran. The material was assigned the structure of 1,4-dimethoxy-5,6-(2,3-dibenzofurano)-2,3-dioxane (IIIb) on the basis of its infrared spectrum and elemental analysis.

The peracetal was decomposed in boiling aqueous sodium hydroxide to give, after acidification, a good yield of a cyclic aldehyde acid (IVa), as the only product. Crystallization from aqueous acetone gave a 91% yield of purified aldehyde acid. This material was assigned the structure of 2-(or 3-)formyldibenzofuran-3-(or -2-)carboxylic acid (IVa) on the basis of its infrared spectrum, neutralization equivalent, and elemental analysis. This aldehyde acid fails to react with 2,4-dinitrophenylhydrazine at room temperature, and this, along with the infrared spectrum, indicates that it exists as the cyclic lactol form. Again it is not known whether this material is one isomer or a mixture of the two possible isomers.

A cyclic aldehyde ester (IVb) was only once isolated from a reaction mixture. A methanolic filtrate from the isolation of the peracetal was allowed to stand overnight. Crystallization occurred, yielding a small amount (4%) of aldehyde ester, which melted in a narrow range. This material was assigned the structure of methyl 2-(or 3-)formyldibenzofuran-3-(or -2-)carboxylate (IVb) on the basis of its infrared spectrum and elemental analysis. The infrared spectrum indicated that this aldehyde ester also exists as the cyclic lactol form. Attempts to prepare this aldehyde ester by refluxing the peracetal (IIIb) for 18 hr. in methanol which had been saturated with dry hydrogen chloride gas were unsuccessful. The product obtained melted lower, and over a wide range, although the infrared spectrum was very similar to that of the authentic material. A similar result was obtained by esterification of the aldehyde acid (IVa) in methanol. It is postulated that these low-melting solids are a mixture of the two possible position isomers of the aldehyde ester. For unknown reasons, apparently a single isomer was isolated originally in the one experiment.

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(3) In two exploratory tests, we found that dibenzofuran was resistant to attack by ozone. In chloroform at −20°, using 1 mole equivalent of ozone, 90% of the starting material was recovered. In methanol at room temperature, using 3.2 mole equivalents of ozone, a 71% recovery was obtained. The reaction products were not identified.

(4) R. Criegee, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **18**, 111 (1957).

(5) (a) P. S. Bailey and F. J. Garcia-Sharp, *J. Org. Chem.*, **22**, 1008 (1957); (b) R. H. Callighan and M. H. Wilt, *ibid.*, **26**, 5212 (1961).

Finally, a dicarboxylic acid (V) was obtained in 25% yield by an alkaline hydrogen peroxide oxidation of an ozonolysis reaction mixture. The purified product was assigned the structure of dibenzofuran-2,3-dicarboxylic acid (V) on the basis of its neutralization equivalent and elemental analysis.

Attempts to isolate and identify products other than those described above were unsuccessful. The remaining material was an intractable, viscous oil with an odor somewhat similar to that of methyl salicylate. The infrared spectrum of this oil indicated that it was probably a complex mixture of materials.

Experimental

The β-brazan used in this work was a commercial material estimated to be 97–98% pure. The methanol and carbon tetrachloride were ACS reagent grade. All melting points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Infracord Model 137 infrared spectrophotometer fitted with a sodium chloride prism. Elemental analyses were performed by the Mellon Institute Microanalytical Laboratory and the Galbraith Laboratories, Knoxville, Tenn. Other reagents mentioned were of the purest quality obtainable. The ozonator and accessory equipment have been described previously.[6]

1-(or 4-)Hydroxy-4-(or -1-)methoxy-5,6-(2,3-dibenzofurano)-2,3-dioxane (IIIa).—A fine suspension of β-brazan (10.9 g., 0.05 mole) in a mixture of 200 ml. of carbon tetrachloride and 100 ml. of methanol was treated with an oxygen stream containing approximately 5 wt. % ozone at −25° (Dry Ice–ethanol bath) and at a flow rate of 17 l./hr. for 4.5 hr. Under these conditions, 5.05 g. (0.105 mole) of ozone was passed into the mixture. Some ozone escaped unabsorbed during the last 0.5 hr. After flushing with oxygen, the cold reaction mixture gave a positive test for hydroperoxide. The solvent was then removed in a flash evaporator under reduced pressure at 30° and the residue was treated with 50 ml. of methanol. After 15 min., the white solids were removed by filtration, washed with *n*-heptane, and dried in a vacuum desiccator. A 4.6-g. (34%) yield of crude 1-(or 4-) hydroxy-4-(or -1-)methoxy-5,6-(2,3-dibenzofurano)-2,3-dioxane, melting at 138–153°, was obtained. The crude material was difficult to purify owing to decomposition; however, several triturations with acetone gave a small amount of purified material, m.p. 163–164°. The infrared spectrum showed a strong hydroxyl band at 2.9 μ but no carbonyl band.

Anal. Calcd. for $C_{15}H_{12}O_5$: C, 66.16; H, 4.44; OCH_3, 11.40. Found: C, 66.22; H, 4.56; OCH_3, 11.62.

1,4-Dimethoxy-5,6-(2,3-dibenzofurano)-2,3-dioxane (IIIb).—β-Brazan was ozonized as described above. After flushing with oxygen, the solvent was removed in a flash evaporator under reduced pressure at 30°. The residue was treated with 50 ml. of methanol, saturated with dry hydrogen chloride, and allowed to stand at room temperature overnight. The white solids were removed by filtration, washed with methanol, then with *n*-heptane, and dried in a vacuum desiccator. A 5.2-g. (36%) yield of 1,4-dimethoxy-5,6-(2,3-dibenzofurano)-2,3-dioxane, m.p. 181–183°, was obtained. On recrystallization from tetrahydrofuran, the product melted at 182–183°. The material gave a slow but definite active oxygen test with potassium iodide. The infrared spectrum did not show a hydroxyl or carbonyl band, but it showed ether bands at 7.5 and 9.0 μ. Although concentrated hydrochloric acid also catalyzes the conversion of hemiperacetal to peracetal, the yield was lower than that obtained using the anhydrous gas.

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.14; H, 4.93; OCH_3, 20.95. Found: C, 67.22; H, 4.84; OCH_3, 20.68.

2-(or 3-)Formyldibenzofuran-3-(or -2-)carboxylic Acid (IVa).—A mixture of IIIb (4.7 g.) and 200 ml. of 2.5% aqueous sodium hydroxide was refluxed for 30 min., during which time solution occurred. The resulting light yellow solution was acidified with concentrated hydrochloric acid while hot. Precipitation occurred, and the solids were removed by filtration, washed with water, and dried in vacuum desiccator. The product was crystallized from 300 ml. of aqueous acetone (1:1). A 3.6-g. (91%) yield of 2-(or 3-)formyldibenzofuran-3-(or -2-)carboxylic acid melting at 202–205° was obtained. The infrared spectrum showed a hydroxyl band at 2.9 and a single carbonyl band at 5.7 μ. The aldehyde acid fails to react with 2,4-dinitrophenylhydrazine solution at room temperature, indicating that it exists in the cyclic lactol form. Similar results were obtained by starting with a crude mixture of IIIa and IIIb melting at 170–175°.

Anal. Calcd. for $C_{14}H_8O_4$: C, 70.00; H, 3.35; neut. equiv., 240. Found: C, 70.05; H, 3.48; neut. equiv., 241.

Methyl 2-(or 3-)Formyldibenzofuran-3-(or -2-)carboxylate (IVb).—This aldehyde ester was isolated in only one experiment, and the results could not be duplicated. β-Brazan was ozonized as previously described. After flushing with oxygen, the turbid, yellow reaction mixture was poured into a 600-ml. beaker, 2 ml. of concentrated hydrochloric acid was added, and the mixture was allowed to stand at room temperature overnight. Filtration gave a 1.6-g. yield (11%) of IIIb, m.p. 180–182°. The solvent was removed in a flash evaporator under reduced pressure at 30° and the residue was treated with 50 ml. of methanol. Filtration gave an additional 1.7-g. yield (12%) of crude IIIb melting at 150–163°. Concentrated hydrochloric acid (2 ml.) was added to the methanolic filtrate and the mixture was allowed to stand overnight. Precipitation occurred, and the product was removed by filtration, washed with a little methanol, and dried in a vacuum desiccator. A 0.5-g. yield (4%) of methyl 2-(or 3-) formyldibenzofuran-3-(or -2-)carboxylate, m.p. 205–207°, was obtained. The infrared spectrum showed a single carbonyl band at 5.7 and a band at 7.5 μ which seems to be typical for methyl ethers. Attempts to prepare this aldehydic ester by refluxing IIIb for 18 hr. in methanol which had been saturated with dry hydrogen chloride were unsuccessful. Instead, the product obtained melted at 157–163°, although the infrared spectrum was very similar to that of the authentic material. A similar result was obtained by esterification of IVa in methanol. It is postulated that these low-melting solids are a mixture of the two possible position isomers of the aldehyde ester. For unknown reasons, apparently a single isomer was isolated in the original experiment.

Anal. Calcd. for $C_{15}H_{10}O_4$: C, 70.86; H, 3.96; OCH_3, 12.20. Found: C, 70.61; H, 4.03; OCH_3, 12.43.

Dibenzofuran-2,3-dicarboxylic Acid (V).—A fine suspension of β-brazan (10.9 g., 0.05 mole) in a mixture of 200 ml. of methylene chloride and 100 ml. of methanol was treated with an ozone–oxygen stream (70 mg. O_3/l.) at room temperature and at a flow rate of 44 l./hr. for 95 min. Under these conditions, 4.87 g. (0.102 mole) of ozone was passed into the reaction mixture. Most of the solids dissolved, and an orange solution remained after ozonolysis. The solvent mixture then was removed in a flash evaporator under reduced pressure at 30° and the solid residue was refluxed for 30 min. with 200 ml. of 2.5% aqueous sodium hydroxide. After cooling to room temperature, the mixture was filtered, yielding 2.7 g. (25% recovery) of crude β-brazan, which was identified by its infrared spectrum. The alkaline filtrate was heated to incipient boiling, 20 ml. of 30% hydrogen peroxide was added, and the mixture was stirred 30 min. An additional 20 ml. of 30% hydrogen peroxide was added then and the stirring was continued 30 min. longer. After cooling to room temperature, the mixture was filtered to remove a small amount of undissolved solids and was made acidic with concentrated hydrochloric acid. A fine precipitate resulted and was agglomerated by heating. The solids were removed by filtration, washed with water, and dried in a vacuum desiccator. A 4.0-g. yield (41% based on the β-brazan consumed) of crude dibenzofuran-2,3-dicarboxylic acid, m.p. 282–290°, was obtained. Crystallization of this crude material from an acetone–water mixture (2:1) gave a 2.4-g. (25%) yield of material, m.p. 291–293°.

Anal. Calcd. for $C_{14}H_8O_5$: C, 65.62; H, 3.15; neut. equiv., 128.0. Found: C, 65.64; H, 3.35; neut. equiv., 128.3.

Acknowledgment.—This work was performed by the Coal Chemicals Research Project, sustained by the United States Steel Corporation, to whom the authors are grateful for permission to publish these results. The assistance of Mr. J. R. Harris in the obtaining of infrared spectra is gratefully acknowledged.

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