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SYNTHESIS OF ISOMERS OF EUGENOL

by

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SYNTHESIS OF ISOMERS OF EUGENOL[1]

Abstract

To correlate the structure and reactivity of eugenol isomers, *o*-eugenol, 2-methoxy-3-allylphenol and chavibetol have been synthesized. A number of routes to prepare 2-methoxy-3-allylphenol have been investigated and a five step synthesis was found to be most suitable. A number of new intermediates and derivatives have been prepared and characterized. An improved separation of chavibetol in chavibetol-eugenol mixtures using a gas chromatographic technique has been achieved. The chelating reaction with zinc oxide to form cementitious products is considerably slower than the vicinal substituted isomers (*o*-eugenol and 2-methoxy-3-allylphenol) as compared to those containing asymmetric substituted groups. Besides steric effect of a neighboring allyl substituent group, the chelation reaction is probably also affected by the ionization constant of the isomer.

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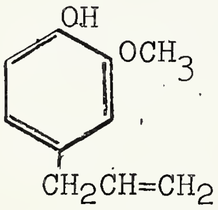
[1] This report covers part of the research conducted at the National Bureau of Standards under the Office of Naval Research Grant - contract ONR P.J.-NR 105-210 (1-29-59).

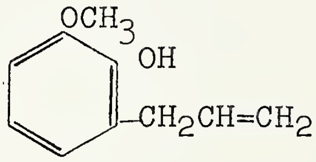
1. INTRODUCTION

Zinc oxide-eugenol cements and impression pastes have found a great number of applications in dentistry. The cements have good marginal sealing properties when compared with other filling materials and are the most innocuous of the filling materials in use today.

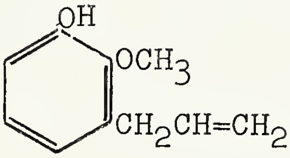
The mechanism of the setting reaction has been investigated in this laboratory [1]. It was found that the hardened mass consists of zinc oxide embedded in a matrix of chelated zinc eugenolate with the empirical formula $(C_{10}H_{11}O_2)_2Zn$. It was the aim of this study to synthesize the position isomers of eugenol (II, III and IV shown below) capable of forming chelates and to investigate the effect of changes in the structure of the isomers on their reactivity with zinc oxide.



eugenol
I

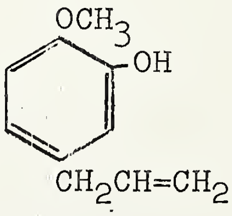


o-eugenol
II



2-methoxy-3-allylphenol

III



chavibetol
(2-methoxy-5-allylphenol)

IV

2. EXPERIMENTAL

2.1 o-Eugenol (II)

o-Eugenol was synthesized by the procedure of Allen and Gates [2] from guaiacol on Claisen rearrangement of the guaiacol allyl ether. Yield = 67% (based on guaiacol). Mixtures of zinc oxide and o-eugenol do not harden readily even in the presence of zinc acetate.

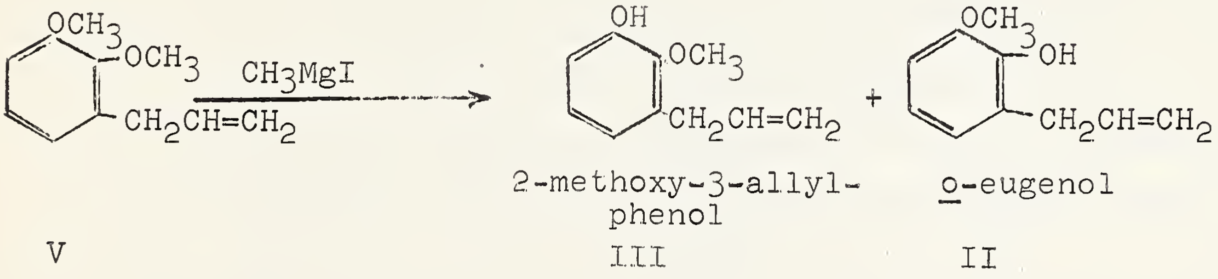
The infra-red spectrum of o-eugenol is shown in Figure 1

2.2 2-Methoxy-3-allylphenol (III)

Three procedures were considered for the preparation of this compound.

2.2.1 Possible Synthesis (Route I)

A synthesis analogous to that described for chavibetol by Hirao [3] and Schöpf and coworkers [4] starting with 2,3-dimethoxy-allylbenzene (V) was briefly investigated.



These studies were soon discontinued since, as will be described below, separation of eugenol from chavibetol proved difficult. However, the later successful separation of eugenol-chavibetol mixtures by gas chromatography indicates that separation of 2-methoxy-3-allylphenol and o-eugenol may be feasible by this technique. Hence, if a gas chromatograph adapted for synthetic work is available, this route appears quite promising.

o-Eugenol benzoate which would be an intermediate in the final separation and purification step was synthesized. o-Eugenol was refluxed with benzoyl chloride both in the absence and presence of pyridine. The reaction mixture was poured into cold water, extracted with ether and the ether solution washed with dilute NaOH and HCl. After drying over anhydrous sodium sulfate, the ether was evaporated. On storage in a refrigerator the residue solidified. After recrystallization from alcohol-water and from ether, the solid melted at 59-60°C.

Anal:[a] Calcd. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0.

Found : C, 76.6; H, 6.0.

The yield of o-eugenol benzoate was low.

2.2.2 Attempted Synthesis (route II)

An attempt was made to synthesize 2-methoxy-3-allylphenol from catechol employing the reaction steps shown on the following page.

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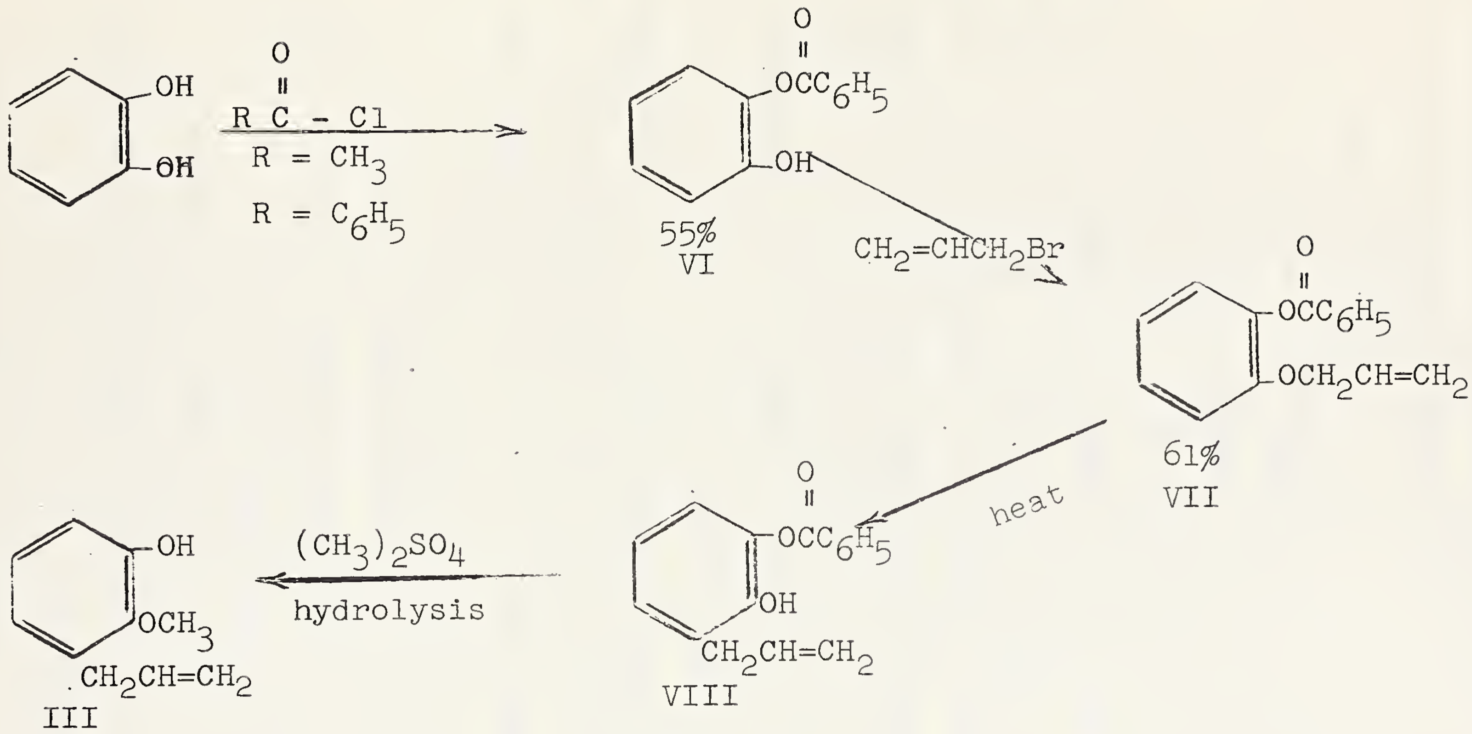
[a] Carbon, hydrogen and nitrogen analyses were done by E. Deardorff, Standard Reference Materials Section, National Bureau of Standards.



Attempted Synthesis of 2-Methoxy-3-allylphenol

2.2.2.1 Catechol Monobenzoate (VI)

Since the yields of monoacetate obtained on reacting catechol with acetyl chloride or acetic anhydride were low, the monobenzoate was prepared according to the procedure of Donadio [5]. 100 g catechol (0.92 mole) and 102 g anhydrous Na_2CO_3 in 1500 ml water were cooled to 6°C and 112 ml benzoyl chloride (136 g, 0.97 mole) were added over 1-3/4 hours with rapid stirring. Stirring was continued for an additional 15 minutes and the cold mixture was filtered and dried. The weight of the crude solid was 235 g and its melting point 85-125°C. On recrystallization from 60:40 (by volume) benzene-petroleum ether and 20:80 (by volume) benzene-petroleum ether or alcohol-water mixtures, 101 g (55%) of pure catechol monobenzoate with M. P. 129-131°C were obtained.

2.2.2.2 2-Benzoyloxyphenyl Allyl Ether (VII)

168 g (0.78 mole) catechol monobenzoate, 110 g (0.80 mole) anhydrous K_2CO_3, 73 ml (103 g, 0.85 mole) allyl bromide were dissolved in 750 ml of reagent grade acetone which had been dried over anhydrous Na_2SO_4. A few glass beads were added to prevent caking of the reaction products and the stirred mixture was refluxed overnight. The cooled mass was dissolved in ether. The ether solution was extracted with 5% NaOH, washed with water, dried over anhydrous Na_2SO_4 and evaporated on a steam bath. The crude ether crystallized on cooling and was purified by recrystallization from an ether-petroleum ether mixture.

Yield: 121 g (61%) M. P. 40-44°C.

On further recrystallization the solid melted at 44°C.

Anal: Calcd. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.6.

Found : C, 75.6; H, 5.7.

2.2.2.3 Rearrangement of 2-Benzoyloxyphenyl Allyl Ether

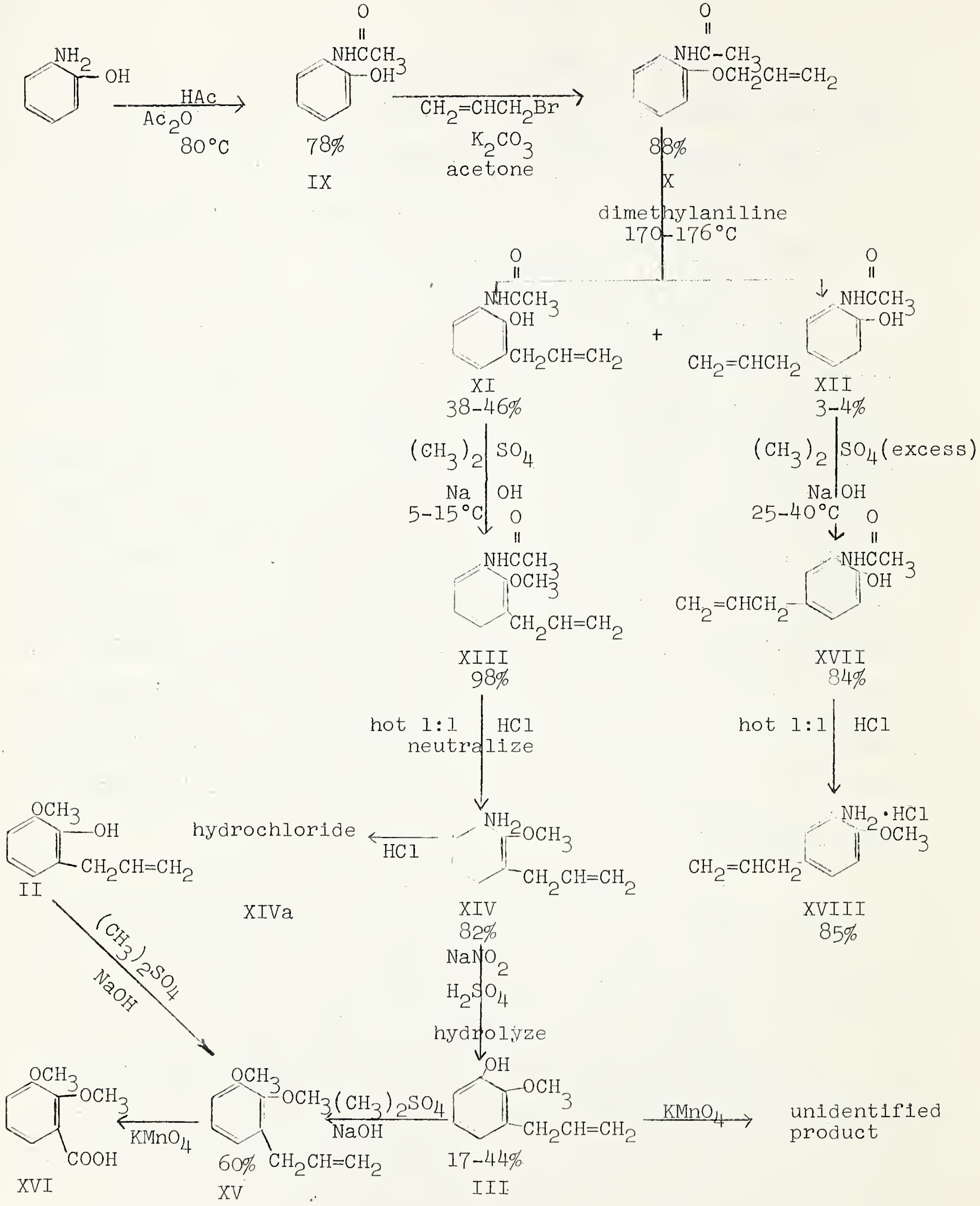
Attempts were made to obtain 2-benzoyloxy-6-allylphenol (VIII) by Claisen rearrangement of the allyl ether. Twelve grams of 2-benzoyloxyphenyl allyl ether were refluxed at 180-200°C for 2-3 hours in the presence and absence of dimethylaniline in a nitrogen atmosphere. The ether solution of the reaction mixture was extracted with 10% NaOH, the aqueous solution was acidified and extracted with ether. On evaporation of the ether, a residue was obtained which consisted mainly of benzoic acid.(2-3 g, 35-52%) and other products which were not identified. No further work on this synthesis or the mechanism of this rearrangement was conducted since route III appeared more promising.

2.2.3 Synthesis by Route III

2-Methoxy-3-allylphenol was synthesized successfully as shown in figure on the following page.

2.2.3.1 *o*-Acetamidophenol (IX)

o-Acetamidophenol was synthesized from 283 g (2.59 mole) *o*-aminophenol (Eastman, practical), 172 ml glacial acetic acid and 296 ml (322 g, 3.15 mole) acetic anhydride according to the procedure of Fierz-David and Kuster [6]. The impure material was filtered and recrystallized in batches from acetone and



Synthesis and Identification of 2-Methoxy-3-allylphenol bone black. Yield: 307 g (78%).

2.2.3.2 o-Acetamidophenyl Allyl Ether (X)

o-Acetamidophenyl allyl ether was synthesized as described by Tiffony [7]. Starting with 250 g of o-acetamidophenol (1.64 mole), 275 g (88% of theoretical yield) of the allyl ether were obtained.

2.2.3.3 2-Acetamido-6-allylphenol (XI) and 2-Acetamido-4-allylphenol (XII)

The Claisen rearrangement was conducted in dimethylaniline at 170-176°C [7] employing 275 g and 439 g of o-acetamidophenyl allyl ether. Refluxing time varied from 1-1/2 to 4 hours. Weight of the isomer mixture was 173 g (63%) for the first run. The two isomers were fractionally recrystallized and separated as described previously [7]. Faster separation was obtained by repeated fractional precipitation similar to the technique of Budesinsky and Rockova [8]. The isomer mixture was dissolved in 1N NaOH and 0.5N H_2SO_4 was added, while stirring, until a few grams of precipitate had formed which were then filtered. Further precipitation took place on addition of H_2SO_4. The purity of the isomers was determined from mixed melting points.

M.P. of 2-acetamido-6-allylphenol = 114-115°C. Yield: 38-46%.

M.P. of 2-acetamido-4-allylphenol = 115-116°C. Yield: 3-4%.

In an attempt to separate the isomers XI and XII more rapidly, the mixture was methylated with dimethyl sulfate. Rapid separation of the isomeric products was not successful.

2.2.3.4. 2-Methoxy-3-allylacetanilide (XIII)

156 g (0.82 mole) of 2-acetamido-6-allylphenol were dissolved in 500 ml water containing 39.2 g (0.98 mole) NaOH. The contents were cooled to 5°C and nitrogen was passed over the solution. One hundred ml (133.2 g, 1.055 mole) of dimethyl sulfate were added with stirring during 1 hour, keeping the solution between 5-12°C. An additional 30 ml (40.0 g, 0.32 mole) dimethyl sulfate were added over a 2-1/2 hour period while the temperature was kept at 15°C. The reaction mixture was heated to room temperature, made basic with dilute NaOH and extracted with ether. The ether extract was washed with water, dried with anhydrous potassium carbonate and the solvent was evaporated off. Nearly colorless flat, needlelike crystals remained. On crystallization from ligroin or 50% ethanol, clear white platelets were formed.

Yield: 163 g (98%). M.P. 86-87°C.

Anal: Calcd. for $C_{12}H_{15}NO_2$: C, 70.3; H, 7.4; N, 6.8.

Found : C, 70.4; H, 7.2; N, 6.9.

2.2.3.5 2-Methoxy-3-allylaniline (XIV) and its Hydrochloride (XV)

46.6 g (0.23 mole) of 2-methoxy-3-allylacetanilide were refluxed with 45 ml of 1:1 HCl (0.27 mole) for 80 minutes. The solution was made alkaline with 10% NaOH and the oily layer was separated. The aqueous layer was extracted with four 25 ml portions of ether. The ether extracts were added to the brown oil. After drying over calcium chloride, the ether was evaporated and the remaining oil distilled at 92-94°C/3.5 mm in the presence of a little hydroquinone. The liquid turned brown on standing in air.

Yield: 30.3 g (82%). $n_D^{25} = 1.553$.

Some product was fractionated in a Piros-Glover spinning band still. B. P. 78-80°C at less than 1 mm pressure.

Anal: Calcd. for $C_{10}H_{13}NO$: C, 73.6; H, 8.0; N, 8.6.

Found : C, 73.5; H, 8.0; N, 8.3.

I. R. Spectrum:[b] The spectrum indicates that little, if any, of the propenyl isomer is present. However, a small fraction which distilled over after the 2-methoxy-3-allylaniline showed a decrease in the intensity of the band at 10 microns which is due to $-CH=CH_2$ groups. If the decrease in the concentration of the allyl compound is due only to the formation of the propenyl isomer, it is mainly the cis isomer which has formed. This is indicated by the band at 13.83 microns which falls in the region in which the cis -CH=CH- group absorbs. That a very low concentration of the trans isomer may also be present is indicated by the very weak band at 10.35 microns which falls in the region in which the trans -CH=CH- group absorbs.

In another run 162 g (0.80 mole) of 2-methoxy-3-allylacetanilide were hydrolyzed for 3-1/2 hours. On vacuum distillation of the product at 10 mm, a considerable amount of a polymer tar remained in the distilling flask.

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[b] I. R. Spectra were determined by Miss Katherine Wharton, Textile Section, National Bureau of Standards.

The hydrochloride was obtained on dissolving 1 g in 15 ml ether and bubbling hydrogen chloride through the solution for five minutes. The white precipitate was recrystallized from hot alcohol containing a drop of concentrated HCl. The white solid melted with decomposition at 178-179°C.

Anal: Calcd. for $C_{10}H_{14}ClNO$: C, 60.2; H, 7.1; N, 7.0.
Found : C, 59.9; H, 7.4; N, 6.9.

2.2.3.6 2-Methoxy-3-allylphenol (III)

2-Methoxy-3-allylaniline was diazotized and the resulting diazonium salt converted to the phenol. Since the yield was rather low, especially when larger quantities of amine were used, a number of runs were conducted using varying reaction conditions. Reverse diazotization appeared to give slightly better yields than the usual addition of sulfuric acid followed by addition of nitrite. Since yields improved when small quantities of diazonium salt were decomposed, 5 g batches of the amine were diazotized. The yield for different batches varied considerably even when the same experimental conditions were employed.

Five g (0.31 mole) of 2-methoxy-3-allylaniline were suspended in 25 ml of water and a solution of 1.15 g of NaOH in 6.5 ml of water was added. This was followed by the addition of 4 g of $NaNO_2$ in 15 ml of water. The solution was added quickly, while stirring, to 4.5 g of concentrated H_2SO_4 which had been cooled previously to 0°C in an ice bath. The temperature during the addition was kept at 0°C. The excess nitrite was decomposed with urea. The cold solution stored in a refrigerator until needed was added slowly from a dropping funnel to a mixture of 150 g of anhydrous sodium sulfate, 100 ml of water and 108 ml of concentrated H_2SO_4 in a three-necked flask equipped for ordinary steam distillation. In later batches the diazotized solution was introduced through a cold finger type addition tube suggested by Lambooy [9] which reached to within 1 cm of the surface of the hydrolysis mixture. The sulfuric acid-sodium sulfate solution was kept at 135-150°C by a surrounding oil-bath and steam was passed through the solution at such a rate that the total volume of liquid remained constant. A considerable amount of tar formed in the flask. The steam distillation was discontinued when colorless clear distillate came over. The distillate was extracted with ether and the combined extracts were washed with 10% $NaHCO_3$ solution. The phenol was then extracted from the ether layer with 10% NaOH and the combined alkaline solutions were acidified, extracted with ether and the ether evaporated off in a partial vacuum. On distillation at 97-99°C/7-10mm, 0.85-2.2 g (17-44%) of 2-methoxy-3-allylphenol, $n_D^{26} = 1.535$, were obtained.

Anal: Calcd. for $C_{10}H_{12}O_2$: C, 73.1; H, 7.4.
Found : C, 72.9; H, 7.3.

I. R. Spectrum (see Figure 1): The spectrum shows absorption bands in the regions in which the $-CH=CH_2$ group absorbs (that is: 5.39-5.55 μ; 7.04-7.09 μ ; 7.69-7.76 μ ; 10.05-10.15 μ ; and 10.93-11.05 μ). [11] The areas in which the <u>trans</u> -CH=CH- group absorbs

(7.67-7.72 μ and 10.31-10.42 μ) fall on the sides of two of these bands, so it is not possible to state with certainty that there is no absorption due to trans -CH=CH- groups. The fact that there is no evidence of an absorption band near 14.49 μ indicates that there is very little, if any, cis -CH=CH- present.

The phenol before the final fractionation contained a considerable amount of ethanol. The mechanism of formation of this product is not known.

2.2.3.7 Conversion to 2,3-Dimethoxybenzoic Acid (XVI)

To establish the identity of the 2-methoxy-3-allylphenol, it was converted to 2,3-dimethoxybenzoic acid (XVI) via 2,3-dimethoxyallylphenol (XV). Approximately 1.5 g (0.09 mole) 2-methoxy-3-allylphenol was dissolved in 2.4 g NaOH in 15 ml of water. While cooling, 2.0 ml dimethyl sulfate were added rapidly and the solution was stirred for 15 minutes. After addition of 2 ml of dimethyl sulfate during 10 minutes, the solution was refluxed for 2 hours, 0.6 g NaOH in 5 ml of water was added and the solution kept at reflux for 2 more hours. The ether extract of the solution was dried over calcium chloride, the solvent was distilled off, and the residue distilled over at 65-68°C/2.5 mm.

Yield: 1.0 g (60%) ($n_D^{25} = 1.524$).

One g of 2,3-dimethoxyallylbenzene was refluxed for 1-1/2 hours with 3.6 g of powdered potassium permanganate dissolved in 40 ml of water. The mixture was filtered through a fritted glass funnel. The filtrate was reduced to about 20 ml, cooled and acidified with 1:4 H_2SO_4. A pale yellow precipitate was filtered off. After recrystallization from benzene and water, the solid material melted at 123-123.5°C. Authentic 2,3-dimethoxybenzoic acid (Aldrich Chemical Co.) and a product obtained on methylation of o-eugenol and subsequent oxidation of the dimethoxy derivative when mixed with this sample gave the same mixed melting point.

An attempted synthesis of 2-methoxy-3-hydroxybenzoic acid by oxidation of 2-methoxy-3-allylphenol with aqueous potassium permanganate was unsuccessful. An acidic compound, soluble in NaOH but insoluble in 5% $NaHCO_3$ and with a melting point over 320°C, was formed.

2.2.3.8 Isomerization by Alcoholic KOH

2-Methoxy-3-allylphenol was refluxed with alcoholic KOH for 16 hours. After evaporation of the alcohol, water was added, the solution extracted with ether and the solvent evaporated. The residue distilled over at 109°C/7mm. (n_D^{25}=1.556). The product appeared to be an impure mixture of cis and trans 2-methoxy-3-propenylphenol as indicated from its infra-red spectrum with the presence of the trans- groups indicated by the band at 10.3μ and that of the cis- groups by the band at 13.9 μ. The presence of some unreacted 2-methoxy-3-allylphenol is also suggested by the absorption band at 10.0 μ and a shoulder at 10.95μ which fall in the region in which $-CH{=}CH_2$ groups absorb.

2.3 Chavibetol

2.3.1 Attempted Synthesis from 2-Acetamido-4-allylphenol (I)

Although the main effort was made to obtain pure chavibetol by the procedure described in the literature [3,4], synthesis from 2-acetamido-4-allylphenol which was obtained as a by-product in the Claisen rearrangement of o-acetamidophenyl allyl ether was also attempted.

2.3.1.1 2-Methoxy-5-allylacetanilide (XVII)

Five g (0.026 mole) of 2-acetamido-4-allylphenol were dissolved in 25 ml of 5.5% aqueous NaOH (0.034 mole). During a 15 min. period, 3.8 ml (5.05 g, 0.04 mole) dimethyl sulfate were added with stirring. Nitrogen was bubbled through the solution to prevent oxidation. During 1-1/2 hours, five 0.6 ml portions of dimethyl sulfate were added intermittently. The pH of the solution was checked at various time intervals and 5 ml portions of the NaOH solution were added whenever the solution had turned acidic. The solution was heated to 40°C for 45 min. and NaOH was added when needed. After cooling, the basic solution was extracted with ether, and the ether extract washed with water and dried over anhydrous potassium carbonate. On evaporation of the solvent and recrystallization from ligroin, long colorless needles (M.P. =56.5-57°C) were obtained. Yield: 4.50 g (84%).

Anal: Calcd. for $C_{12}H_{16}NO_2$: C, 70.3; H, 7.4; N, 6.8.
Found : C, 70.3; H, 7.6; N, 6.5.

I.R. Spectrum: The spectrum shows numerous differences from that of 2-methoxy-3-allylacetanilide (XIII). To what extent these differences are due to the difference in the position of the allyl group is not known.

2.3.1.2 2-Methoxy-5-allylaniline Hydrochloride (XVIII)

To 3.8 g (0.019 mole) 2-methoxy-5-allylacetanilide, 10 ml of 1:1 HCl were added and the mixture was refluxed for 45 min. A slightly yellow solid precipitated out on cooling. The solid was very soluble in H_2O, CH_3OH, C_2H_5OH; soluble in $CHCl_3$ and insoluble in ether, pentane, ligroin and benzene. On recrystallization from a concentrated aqueous solution acidified with a little HCl, colorless needles (M.P.=170-172°C) were obtained.

Yield(including recovery from mother liquor):3.15g (85%)

Anal: Calcd. for $C_{10}H_{14}ClNO$: C, 60.2; H, 7.1; N, 7.0.

Found : C, 60.2; H, 7.2; N, 6.8.

2.3.1.3 Attempted Synthesis of 2-Methoxy-5-allylaniline

Three grams of 2-methoxy-5-allylaniline hydrochloride dissolved in 15 ml water were made basic with 2% NaOH, extracted with ether and, after drying, the solvent was evaporated. A dark liquid remained which sublimed on attempted vacuum distillation, depositing a crystalline compound which, on recrystallization from 70% ethanol and ligroin, gave colorless scales (M.P.=47°C). The presence of an absorption band at 10.32μ suggests that some isomerization to the trans propenyl group has taken place. Since there are no bands around 13.9μ , there appears little if any of the <u>cis</u> isomer present. Elementary analysis for carbon and hydrogen indicates that the compound is impure.

Anal: Calcd. for $C_{10}H_{13}NO$: C, 73.6; H, 8.0.
Found : C, 72.6; H, 8.0.

In another attempt to synthesize the amine, 2-methoxy-5-allylacetanilide was hydrolyzed and, after neutralization, an oil was isolated. On vacuum distillation, a brown solid possibly a polymer was formed which contained nitrogen and was soluble in ethanol, dilute H_2SO_4; insoluble in water, carbon tetrachloride and dilute NaOH.

Since all the 2-methoxy-5-allylacetanilide had been used up, no further attempt was made to synthesize chavibetol by this route.

2.3.2 Synthesis from Eugenol Methyl Ether

Small quantities of chavibetol were obtained by the procedure previously described (3,4).

Eugenol methyl ether (3,4-dimethoxy-1-allylbenzene) was synthesized in 88% yield according to the procedure of Luff, Perkin and Robinson [10]. Demethylation of this compound with Grignard reagent was conducted as suggested by Schöpf and coworkers [4]. Separation of the resulting eugenol-chavibetol mixture by preparation of their potassium salts and formation of the benzoyl esters gave only small amounts of reasonably pure chavibetol benzoate (M.P.=47-48°C) and larger quantities of the lower melting isomer mixtures.

Gas chromatographic separation of the impure eugenol-chavibetol mixtures could be accomplished with a diisodecyl phthalate column heated to 175°C using a hydrogen flame detector. Larger quantities of the isomers were separated using a Beckman chromatograph designed for synthetic work employing an Apiezon J on C 22 firebrick column[c] with a column temperature of 180°C and 10 lbs/in^2 pressure. The detector temperature was kept at 195°C. The infra-red spectrum of chavibetol is shown in Figure 1.

The chavibetol was characterized by conversion to isochavibetol as described by Hirao [3]. The long needles melted at 95-96°C (reported M.P. = 95-96°C).

2.4 Reaction of the Eugenol Isomers with Zinc Oxide

To determine the relative reactivities of the isomers of eugenol capable of chelation, eugenol, o-eugenol and 2-methoxy-3-allylphenol were mixed with zinc oxide.(Not enough chavibetol has been synthesized so far to be included in this study.) o-Eugenol and 2-methoxy-3-allylphenol harden only very slowly, even in the presence of zinc acetate. This reduced activity of vicinal substituted isomers as compared to the asymmetric substituted eugenol shows that the chelation reaction is greatly influenced by steric hindrance of neighboring allyl groups. Studies to determine if substitution of metals with smaller atomic radii than zinc will reduce this steric effect would be of interest. Besides steric effects of the substituent groups, the chelation reaction probably also depends on the ionization constants of the isomers. The results of this study would indicate that synthesis of new chelate

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[c] Chromatographic separation was made by R.J. Vanapeldoorn, Walter Reed Institute of Research, Washington 25, D. C.

cements should be directed towards derivatives with asymmetric substituted groups (1,2,4- and 1,2,5-substituted benzene derivatives). Further studies to correlate structures and reactivity of this type of chelating agent with metal oxides appear desirable.

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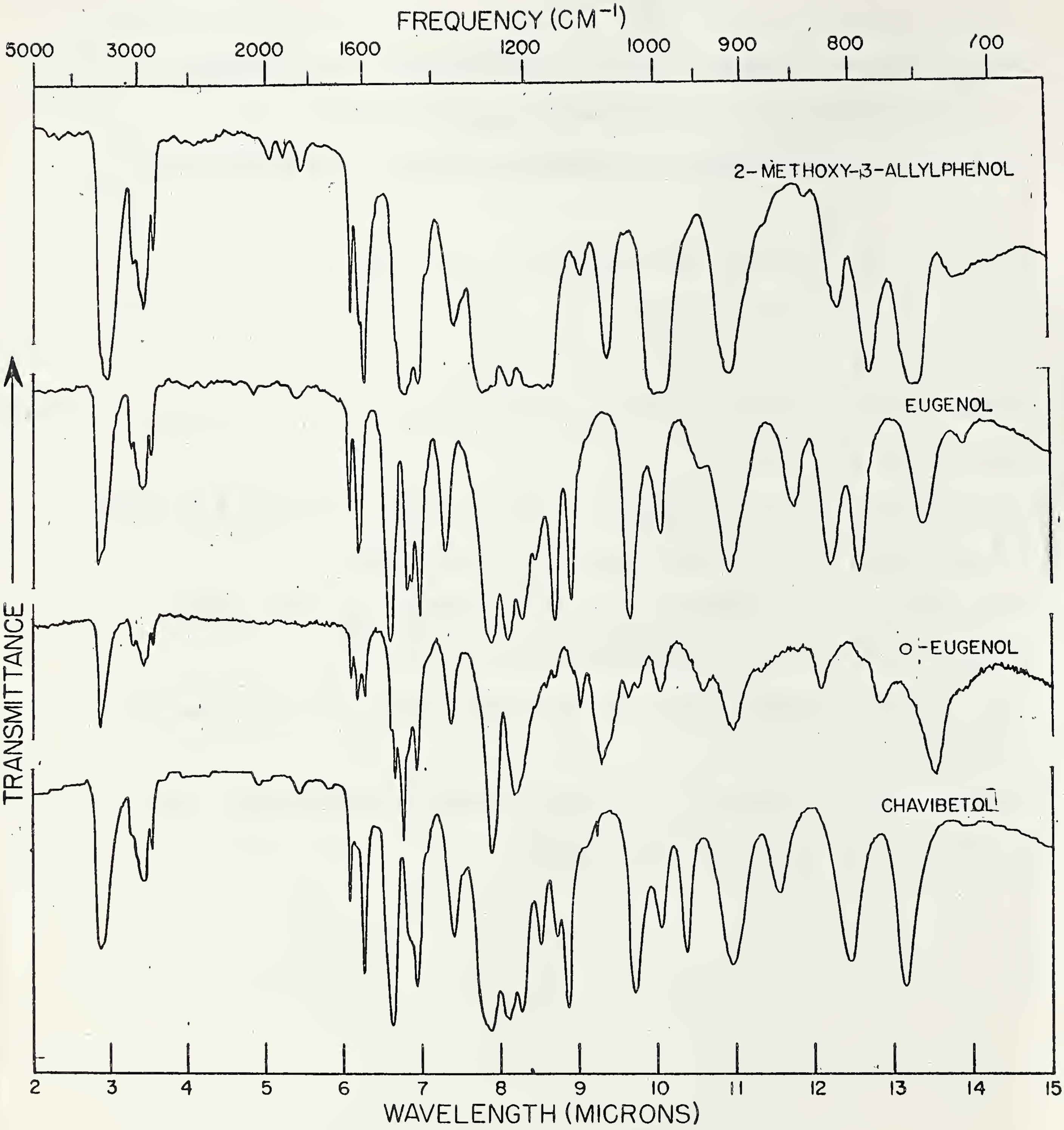

Infra-red Absorption Curves of 2-Methoxy-3-allylphenol, Eugenol, o-Eugenol and Chavibetol.

Figure 1