THE CONVERSION OF EUGENOL INTO ISOEUGENOL.

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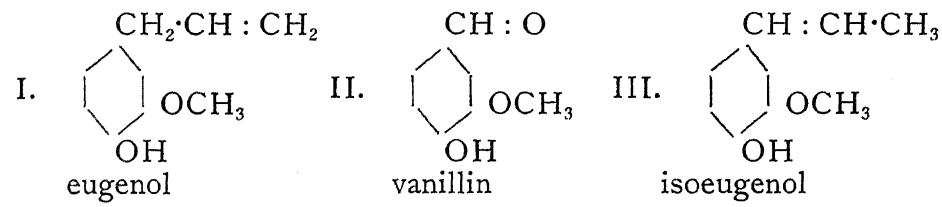
I. INTRODUCTION.

The chief source from which synthetic vanillin, protocatechuic aldehyde monomethyl ether, is obtained is 4-hydroxy-3-methoxy-1-allylbenzene or eugenol.

As appreciable amounts of the latter can be obtained in India from the essential oil from the leaves of the cinnamon trees of the West Coast, we took up a systematic study of the conversion of eugenol into vanillin, in order to ascertain the exact details for obtaining good yields at each stage.

The conversion of eugenol into vanillin necessitates the oxidation of the unsaturated allyl, $CH_2 : CH \cdot CH_2 \cdot$, group to the aldehyde group $\cdot CHO$.



The direct oxidation of $\cdot CH_2 \cdot CH : CH_2$ to $\cdot CHO$ is not readily effected, as the tendency is to form $\cdot CH_2 \cdot CHO$ i.e. homovanillin or the corresponding acid, homovanillic acid OCH_3 (OH) $C_6H_3 \cdot CH_2 \cdot COOH$. In order to overcome this difficulty it is usual to convert eugenol into its structural isomeride, isoeugenol, 4-hydroxy-3-methoxy-propenylbenzene (III) and then to oxidise this either in the free form or as its acetyl derivative.

$$CH_3 \cdot CH : CH \cdot C_6H_3(OH)OCH_3 + 3O \longrightarrow$$
$$CHO \cdot C_6H_3 (OH)\ OCH_3 + CH_3 \cdot CO_2H.$$

Our first object has been the study of the conversion of eugenol into its isomeride under different conditions and the elaboration of a method for the rapid estimation of each of these in mixtures of the two. Details of both are given in the present paper.

II. DETERMINATION OF EUGENOL AND ISOEUGENOL IN MIXTURES OF THE TWO.

Miss P. V. McKie[1] describes a method for determining the composition of such mixtures by means of the melting point of the mixed benzoyl derivatives. Both eugenyl and isoeugenyl benzoates are solid, crystalline substances, melting respectively at 69–70° and 103–104°, but the melting point curve of mixtures is unfortunately not of the simple eutectic type as there is a discontinuity. Miss McKie's method has the further drawback that the preparation of the benzoyl derivatives takes some time.

We find that the determination of the refractive index of a mixture of the two phenols affords a simple and quick method for ascertaining the percentage of each constituent, if the graph representing the relation between refractive indices and composition is known. For the purpose of obtaining such a graph the pure phenols were isolated by hydrolysing their pure acetyl derivatives and mixtures of known composition made.

Preparation of pure materials. Eugenol was dried over anhydrous sodium sulphate and distilled under a pressure of 6 mm. The fraction boiling at 116–118° was collected and then acetylated by means of acetic anhydride in the presence of pyridine. The acetyl derivative is an oil boiling at 137–138° under a pressure of 5 mm., and was hydrolysed by boiling for three hours with a 5 per cent. aqueous sodium hydroxide solution. The recovered eugenol boiled at 116–117° under a pressure of 6 mm. and was again acetylated and the acetyl derivative distilled and hydrolysed.

Eugenol (40 grams) was converted into its isomeride by fusion for 5 minutes at 220° with potassium hydroxide (160 grams). The recovered oil boiled at 124–126° under a pressure of 5 mm. and when acetylated by the pyridine method gave a solid acetate which crystallized from a mixture of benzene and light petroleum in slender crystals melting at 80–81° [2]. This pure acetyl derivative was hydrolysed by means of a boiling 5 per cent. aqueous potassium hydroxide solution and the liberated phenol had the properties given in Table I.

[1] *J. Chem. Soc.*, 1921, **119**, 777.
[2] Tiemann gives the melting point as 79–80° (Ber., 1891, **24**, 2873).

TABLE I.

Properties of Eugenol and Isoeugenol.

—	Eugenol	Isoeugenol
Boiling point 6 mm.	116–117°	123—124°
Refractive index at 30°	1·53664	1·57237
Density	1·062 (23°)	1·094 (22°)

In Table II are given the results of earlier determinations of the refractive indices by other authorities.

TABLE II.

Refractive Indices.

Authority	Eugenol		Isoeugenol	
	Observed	Corrected to 30°	Observed	Corrected to 30°
Eykman[1]	1·5439 at 14·5°	1·5377	1·5680 at 18°	1·5632
Tiemann[2]	1·5438 at 14·5°	1·5376	1·5728 at 18°	1·5680
Gildemeister and Hoffmann[3]	1·541 to 1·542 at 20°	1·537 to 1·538	1·570 to 1·576 at 20°	1·566 to 1·572
Allen[4]	1·5400 at 20°	1·5360	.....	.....

For the determination of the refractive indices a Pulfrich refractometer was used.

Table III gives the results of determinations of the temperature co-efficient for the refractive indices of both eugenol and isoeugenol and the mean value is 0·0004 per rise of 1°c. Warm water was circulated round the prism and the measurement made only when the temperature remained constant for three minutes.

[1] *Ber.* 1890, **23**, 862.
[2] *Ibid.*, 1891, **24**, 2870.
[3] *Die aetherischen Oele* 1910, vol. i. 501 and 503.
[4] *Commercial Organic Analysis*, 1911, vol. iv, 293.

TABLE III.

Temperature co-efficients for n_D

Refractometer reading	n_D	Temperature	Co-efficient for 1°
Eugenol—			
30° 38′	1·53648	29·7	—
30° 50′	1·53549	32·1	— 0·00041
31° 1′	1·53457	34·3	— 0·00042
31° 8′	1·53398	35·8	— 0·00041
Isoeugenol—			
22° 30′	1·57289	28·7	—
22° 52′	1·57144	32·4	0·00039
23° 13′	1·57004	35·8	— 0·00040

Determination of refractive indices of mixtures of eugenol and isoeugenol of known composition.

About five grams of the one component was carefully weighed in a stoppered weighing botle, a little of the other component was added and the whole re-weighed. The contents were well mixed with a glass rod and a sample removed for examination. After the determination of the refractive index the bottle was again weighed and, knowing the loss in weight, the amount of each constituent present in the mixture was calculated. To prepare the second mixture of known composition the requisite quantity of the second component was calculated and a measured number of drops of that ingredient was added to the mixture, the bottle re-weighed and the percentage composition calculated. The procedure was repeated until the mixture contained practically equal amounts of the two constituents. Four series of experiments were made giving concordant results.

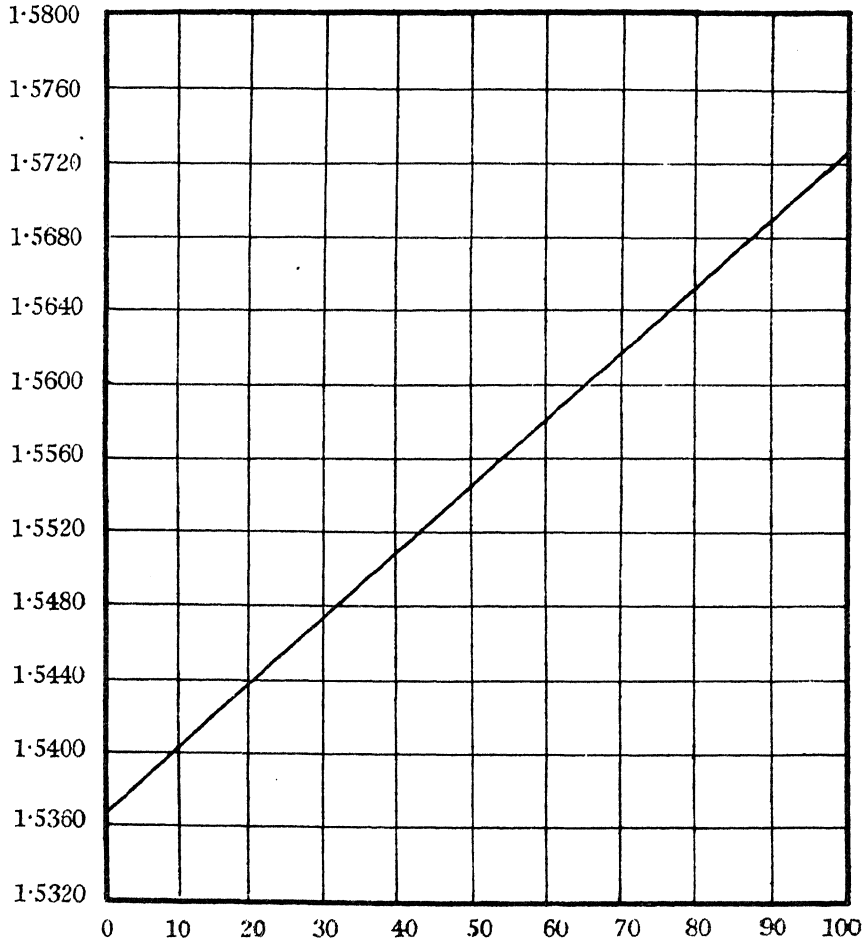
By plotting the percentage composition against the refractive index a graph showing the relation between the two was obtained. The graph is a straight line indicating that the function is linear.

This graph has been utilised for ascertaining the composition of mixtures of the two isomerides obtained in the subsequent experiments.

The calculation is only valid in the absence in the distillate of compounds other than the two eugenols. This assumption appears to be justified, as in certain experiments nearly pure Eugenol was the only volatile product and in others pure isoeugenol. The impurities present in the products appear to be non-volatile and remain in the flask, as the distillate obtained boiled within a range of 4°, and further heating the residue gave no more distillate.

FIGURE I.

Refractive Index of Mixtures of
Eugenol and Iso-eugenol.



Percentage of Iso-eugenol.

The following Table, No. IV, shows the values obtained :—

TABLE IV.

Refractive Index of Mixtures of Eugenol and Isoeugenol.

Experiment No.	Grams of		Percentages in mixture		$n_D^{30°}$
	Eugenol	Isoeugenol	Eugenol	Isoeugenol	
—	...	...	100·0	...	1·53664
1*d*	4·9246	0·5906	89·3	10·7	1·54074
2*d*	4·3750	1·1288	79·5	20·5	1·54406
3	4·6569	2·0807	69·1	30·9	1·54764
3*d*	3·6893	1·9609	65·3	34·7	1·54911
4	4·5171	3·0362	59·8	40·2	1·55142
4*d*	3·1799	2·5633	55·4	44·6	1·55254
5	4·4004	4·4749	49·6	50·4	1·55438
9	2·7918	4·2780	39·5	60·5	1·55819
8	2·0846	4·9290	29·7	70·3	1·56176
6*d*	1·4833	4·3109	25·6	74·4	1·56320
7	1·3642	5·6235	19·5	80·5	1·56541
5*d*	0·8806	4·9820	15·02	84·98	1·56709
6	0·6894	6·3639	9·8	90·2	1·56888
—	...	...	...	100·0	1·57237

III. CONVERSION EXPERIMENTS.

There appear to be three main methods for the conversion of eugenol into its isomeride.

(*a*) G. deLaire[1] states that isoeugenol may be prepared by heating eugenol with potassium hydroxide in amyl alcoholic solution during 16 to 24 hours. After removal of the amyl alcohol by steam distillation the residue is acidified and the oily layer of isoeugenol separated by decantation, then washed and finally distilled. A similar method is described by Tiemann,[2] who heated 5 parts of eugenol with 12·5 parts of potassium hydroxide and 18 parts of pure amyl alcohol for 16 to 20 hours at 140°.

(*b*) Einhorn and Frey[3] state that isoeugenol can be prepared by heating one part of eugenol with four parts of potassium hydroxide and a little water at 220°.

(*c*) German Patent No. 179948 by Fritze and Co.[4] claims that when the potassium salt of eugenol is heated in a vacuum or in an

[1] *J. Soc. Chem. Ind.*, 1891, **10**, 854, Eng. Pat. 17547 of November 1, 1890.
[2] *Ber.* 1891, **24**, 2870.
[3] *Ibid.*, 1894, **27**, 2455.
[4] *Chem.* Zentr. 1907, *i*, 434.

atmosphere of an indifferent gas at temperatures between 190° and 220°, and in the absence of excess of alkali or of any solvent, isomerisation occurs.

The experiments which we have carried out may be classified as follows :—

A. *Fusion experiments* :—

1. Fusions with caustic soda.
2. Fusions with caustic potash.
3. Fusions with mixtures of the two alkalis.
4. Fusions with caustic potash in the presence of paraffin.

B. *Heating the potassium salt of eugenol in an atmosphere of nitrogen.*

C. *Autoclave experiments with a 50 per cent. aqueous solution of potassium hydroxide.*

A. Fusion Experiments.

General method of procedure.—

The requisite amount of powdered caustic alkali, usually four times the weight of the phenol,[1] was weighed in a nickel crucible, the eugenol (usually 30 grams) added and the whole well mixed. The crucible was placed in an oil bath heated to 140° and the temperature raised rapidly to that required, an operation which usually took 10 to 15 minutes. The contents of the crucible were well stirred by means of a nickel rod during the whole course of heating and thermometers were inserted in the oil bath and also in the caustic alkali mixture.[2] At the end of the given time the crucible was removed from the bath, allowed to cool, the product dissolved in water and decomposed with sulphuric acid. The liberated phenol was extracted with ether, the etheral solution shaken with water, dried over anhydrous sodium sulphate and the ether removed, finally under reduced pressure. The oil so obtained is termed the 'crude yield' and the same product after distillation under reduced pressure 'pure yield'.

[1] This proportion is roughly 1 mol. of eugenol for 11 mols. of potassium hydroxide or 15·5 mols. of sodium hydroxide.

[2] The second thermometer was placed in a hard glass tube sealed at one end and containing mercury.

A low crude yield usually indicates the formation of resinous products insoluble in ether, and a high crude yield but a low 'pure yield' the formation of products soluble in ether but non-volatile even under reduced pressure. The refractive index of the oil after distillation was determined and the percentage of isoeugenol ascertained from the graph.

The results of four series of fusion experiments are given in Tables V to VIII. The experiments were in most cases carried out in duplicate.

I. FUSIONS WITH SODIUM HYDROXIDE.

TABLE V.

Fusions with Sodium Hydroxide.

Experiment No.	11	10
Temperature	200°	210°
Time in minutes	15	15
Crude yield per cent. ...	66·5	76·2
Pure yield per cent.	53·3	63·5
Boiling point and Pressure ...	241-242° 684 mm.	242-244° 685 mm.
$n_D^{30°}$	1·5380[1]	1·5374

They show that with caustic soda there is appreciable decomposition and practically no conversion of eugenol to isoeugenol.

2. POTASSIUM HYDROXIDE FUSIONS.

The results obtained by using different amounts of potassium hydroxide at 220° and also the effect of varying the time are given in Table VI.

The results indicate that when the potassium hydroxide is reduced from 4 to 3 or 2·5 times the weight of the eugenol, the yield of ether soluble products is diminished (cf. crude yields), but the yield of ether soluble non-volatile products is unaffected (cf. residues).

[1] The value for eugenol is 1·5366 and for isoeugenol 1·5724.

TABLE VI.

Fusions with Potassium Hydroxide.

Experiment No.	Hand Stirring				Mechanical Stirring	
	23	37,38	39,40	41,42	67,68	69,70
Parts by weight of potassium hydroxide to 1 pt. of eugenol	4	3·5	3	2·5	3	3
Temperature	220°	220°	220°	220°	220°	220°
Time in minutes ...	5	5	5	5	20	40
Crude yield, per cent. ...	96	95	92	89	94	92
Pure yield per cent. ...	85	82	80	79	83	81
Boiling point	119-121°	123-127°	123-128°	123-126°	124-126°	125-127°
Pressure in mm. ...	4	7	7	6	6	6
Residue per cent. ...	11	11	11	11	10	9
$n_D^{30°}$	1·5724	1·5720	1·5705	1·5668	1·5710	1·5718
Per cent. of Isoeugenol from graph	100	99	94·5	84	97·2	99
Actual recovery of Isoeugenol from 100 gms of Eugenol	85	80	75	66	80·5	80·4

The conversion into isoeugenol is also affected by a diminution in the amount of alkali used. A few experiments made using mechanical stirring show that slightly higher results can be obtained by this device.

3. FUSIONS WITH MIXTURES OF SODIUM AND POTASSIUM HYDROXIDES.

In all experiments the amount of total alkali used was four times the weight of eugenol. Only the proportions of the two alkalis in the mixtures were changed.

Table No. VII gives the results of several experiments made under the same conditions of temperature and time, viz., 220° and five minutes, the variant being the relative proportions of caustic soda and potash.

The effect of increasing the proportion of sodium hydroxide is to reduce the 'crude yield' to about 90 per cent., to effect also an appreciable diminution in the pure yield and further to lessen the percentage conversion so that the distilled phenol contained appreciable amounts of unaltered eugenol.

TABLE VII.

Fusions with Mixtures of Sodium and Potassium Hydroxides.

Experiment No.	Hand Stirring					
	23	27,32	28,29	30,31	33,34	35,36
KOH : NaOH	1 : 0	1 : 1	1 : 2	1 : 3	1 : 4	1 : 5
Temperature	220°	220°	220°	220°	220°	220°
Time in minutes ...	5	5	5	5	5	5
Crude yield per cent. ...	96	96	93	90	90	90
Pure yield per cent. ...	85	82	78	75	71	67
Boiling point	119–121°	124–127°	124–126°	125–127°	125–128°	124–126°
Pressure in mm. ...	4	6	6	7	6	6
Residue per cent. ...	11	12·5	13	14	18	20
$n_D^{30°}$	1·5724	1·5712	1·5710	1·5684	1·5641	1·5614
Per cent. of Isoeugenol from the graphs	100	96·5	96	89	76·5	69
Actual recovery of Isoeugenol	85	79	75	67	54	46

TABLE VIII.

Fusions with a Mixture of Sodium Hydroxide and Potassium Hydroxide, 2 : 1.

Experiment No.	Hand Stirring							Mechanical Stirring	
	49,50	51,52	55,56	53,54	57,58	59,60	61,62	63,64	65,66
Temperature.	200°	200°	200°	210°	210°	210°	210°	210°	210°
Time in minutes ...	20	40	80	20	40	80	120	20	80
Crude yield per cent. ...	94	93	95	94	94	94	93	93	93
Pure yield per cent. ...	81	81	81	82	83	82	81	82	82
Boiling point.	124–126°	125–128°	124–128°	123–127°	124–128°	122–126°	121–125°	153–155°	130–133°
Pressure in mm. ...	6	7	7	6	7	5	5	19	10
Residue per-cent. ...	11	11	11	11	10	11	11	11	11
$n_D^{30°}$	1·5697	1·5700	1·5698	1·5688	1·5704	1·5715	1·5718	1·5703	1·5721
Per cent. Iso-eugenol ...	93	93	92·5	90	94	97·3	98·2	94	99·5
Per cent. re-covery of Isoeugenol.	75	75	74	74	78	80	79	77	81

Comparing the experiments in Tables VI and VII it is evident that the experiment No. 41 in which two and a half parts by weight of potash were used is inferior not only to experiment No. 27 in which the 1 : 1 mixture was used but also to experiments Nos. 28 and 30.

In Table VIII are given the results of a series of experiments made with a mixture of one part of caustic potash and two parts of caustic soda at temperatures of 200° and 210°. At 200° the maximum percentage of isoeugenol in the final mixture is 93 per cent. and the amount is not affected by increasing the time of fusion.

The best results are obtained for 80 minutes at 210° using mechanical stirring, when an 81 per cent. yield of practically pure isoeugenol is obtained.

4. EXPERIMENTS WITH PARAFFIN OIL AS A DILUENT FOR ALKALI.

A recent patent by F. W. Atack and J. Anderson,[1] for 'Improvements in and relating to the fusion of Organic substances with alkalis' claims improvement in the efficiency of fusion process by increasing the yield of the desired product or decreasing the quantity of undesirable bye-products. It also claims to provide processes whereby caustic soda can be used effectively instead of caustic potash for fusions of some organic substances by using a very high boiling oil such as liquid paraffin as a diluent.

Three different experiments were made using liquid paraffin along with alkali. The amount of paraffin oil used was equal in weight to the amount of the alkali used. The results were not found to be any better than those given by other experiments under the same conditions without the use of paraffin oil as may seen from Table IX.

B. Heating the Potassium salt of Eugenol in an Atmosphere of Nitrogen.

A series of experiments based on Fritze and Co.'s patent (p. 245) has been made, but the results obtained at 220° indicate no transformation into isoeugenol. The indifferent gas used was nitrogen and it was prepared by the method given in Travers' Study of Gases. The potassium salt of eugenol was prepared by adding the calculated

[1] Indian Patent Specification No. 6694, 1st March, 1921.

TABLE IX.

Fusions in presence of liquid paraffin.

Experiment No.	44	47, 48	45, 46
Alkali used	KOH 3·5	KOH 1·33 ; NaOH 2·66	KOH 1 ; NaOH 3
Temperature	220°	220°	220°
Time in minutes ...	5	5	5
Crude yield per cent. ...	91	89	87
Pure yield per cent. ...	79	75	74·3
Boiling point	125-127°	123-127°	126-129°
Pressure in mm.	6	6	7
Residue per cent. ...	11	11	11
$n_D^{30°}$	1·5628	1·5717	1·5681
Per cent. Isoeugenol from the graph	73	97·7	87·7
Actual recovery of Isoeugenol	58	73	65

amount of aqueous potassium hydroxide to eugenol and removing the water at a comparatively low temperature under reduced pressure.

A weighed quantity of the finely powdered salt was placed in a wide-mouthed, round-bottom flask of 300 cc. capacity and immersed to its neck in an oil-bath.

A thermometer placed in the oil registered the temperature. Before the oil was heated a slow stream of nitrogen was passed through the flask for twenty minutes to remove the air, and the stream was kept up during the whole time of heating.

After the heating was over, the mass was removed from the flask by warm water acidulated with a little sulphuric acid and decomposed by a dilute solution of sulphuric acid (1 : 3) and the liquid extracted with ether. The extract after being washed completely free of acid was kept to dry over anhydrous sodium sulphate. After evaporation of the ether, the crude yield obtained was weighed and distilled under reduced pressure. The results of these experiments are given in Table X.

TABLE X.

Experiment No.	71	72	73	74
Temperature ...	220°	190°	200°	200°
Time in minutes ...	15	30	60	300
Crude yield per cent. ...	92	94	93	93
Pure yield per cent. ...	47	80	80	21
Boiling point ...	129-131°	114-116°	115-119°	139-143°
Pressure in mm. ...	11	6	6	18
$n_D^{30°}$	1·5370	1·5366	1·5372	1·5379

$n_D^{30°}$ for eugenol is 1·5366.

C. Autoclave Experiments.

Several attempts were made to convert eugenol into its isomeride by heating with a 50 per cent. aqueous solution of potassium hydroxide in an autoclave. As the autoclave at our disposal was rather large the mixture was not placed directly in the autoclave but in a covered nickel crucible, which was placed on the bottom of the autoclave and surrounded by a 50 per cent. aqueous solution of potassium hydroxide. The product was removed when the temperature had fallen to 75° and the phenols isolated as in the earlier experiments.

Tables XI, XII and XIII give the results obtained when different proportions of eugenol and alkali were used.

TABLE XI.

Eugenol : Potassium Hydroxide = 1 : 2 (by weight).

Experiment No.	75	84	96	91	90	97	85,92
Temperature	203°	185°	177°	174°	174°	174°	174°
Time in minutes	15	15	30	15	30	45	60
Pressure lbs. per sq. in. ...	90	61	50	50	48	48	48
Crude yield per cent. ...	96	96	96	96	96	95·4	96
Pure yield per cent. ...	51	73	81	82	80	74	70
Boiling point	127-129°	124-128°	121-125°	125-129°	129-133°	124-128°	128-130°
Pressure in mm.	7	6	5	6	9	6	8
Residue per cent.	...	21	13	13	...	28	20
$n_D^{30°}$	1·5721	1·5715	1·5705	1·5678	1·5705	1·5712	1·5712
Per cent. Isoeugenol ...	99·7	98	96	88	96	98	98
Actual recovery per cent. ...	51	67	74	72	77	73	69

TABLE XII.

Experiment No.	113,114	117	115,116
KOH : Eugenol by weight	3 : 1	3 : 1	4 : 1
Temperature	174°	174°	174°
Time in minutes	45	22	45
Pressure lbs. per sq. inch	50	50	50
Crude yield per cent.	96	96·5	96
Pure yield per cent.	77	79·8	79
Boiling Pt.	130°–133°	121°–123°	122°–124°
Pressure in mm.	10	5	5
Residue per cent.	18	15 5	15
$n_D^{30°}$	1·5717	1·5710	1·5720
Percentage of isoeugenol	98·5	96·5	99
Percentage of actual recovery of isoeugenol ...	76	77	78

TABLE XIII.

Eugenol : Potassium Hydroxide = 1 : 1 (by weight).

Experiment No.	99	98	100	102	110	101
Temperature	195°	185°	174°	175°	173°	168°
Time in minutes ...	15	15	15	30	60	15
Pressure lbs. per sq. in. ...	65	56	50	50	48	40
Crude yield per cent. ...	96·3	96·4	96	96·5	96	96·5
Pure yield per cent. ...	63	73	82	78	77	84
Boiling point	129-133°	124-128°	128-133°	129-131°	125-127°	125-130°
Pressure in mm. ...	9	6	8	7	6	7
$n_D^{30°}$	1·5708	1·5715	1·5651	1·5698	1·5702	1·5584
Per cent. Isoeugenol ...	96	97·5	80	93·5	95	61·5
Per cent. actual recovery of Isoeugenol	60	71	66	73	73	51

TABLE XIV.

Experiment No.	105	106	107
Molecular proportions of eugenol to potassium hydroxide	1 : 1	1 : 2	1 : 3
Temperature	173°	174°	173°
Time in minutes	15	15	15
Pressure lbs. per sq. in.	48	48	48
Crude yield per cent.	81	96	96
Pure yield per cent.	68·5	86	84
Boiling point	124-128°	125-128°	122-125°
Pressure in mm.	7	6	5
Residue per cent.	11·5	10	10
$n_D^{30°}$	1·5369	1·5561	1·5655
Per cent. Isoeugenol	...	55	81
Actual recovery per cent.	...	47	68

The results with the lower proportions of potassium hydroxide are not satisfactory.

In experiments Nos. 75 and 84 the yields are low although the product in each case is nearly pure isoeugenol. The yields can be increased by using lower temperatures (e.g., experiments 96, 97) and after 45 minutes the phenol recovered is practically pure isoeugenol.

One noticeable feature in the results of these expreriments is that the percentage of crude yields is the same throughout, viz., 96, while it is only the yield of the pure product that differs with change of conditions. Thus at high temperatures, or with longer time, more non-volatile decomposition products soluble in ether are formed.

It will be seen on comparing Tables XI and XII with Table VI that using 50 per cent. solutions in an autoclave gives almost as good yields with two parts by weight of caustic potash at 174° as can be obtained by fusion with 3·5 parts at 220°, and that autoclaving with 3 parts at 174° is slightly better than fusing with the same amount at 220° unless mechanical stirring is used in the latter case.

IV. SUMMARY.

1. An accurate and rapid method for estimating eugenol and isoeugenol in mixtures of the two has been worked out.

2. The fusion of eugenol with sodium hydroxide, potassium hydroxide and mixtures of the two has been studied.

(*a*) Complete conversion into isoeugenol can be brought about by fusing eugenol with eleven equivalents of potassium hydroxide for five minutes at 220° or with eight equivalents for forty minutes at 220° using mechanical stirring.

(*b*) Fusion with sodium hydroxide at 200-210° produces little or no conversion.

(*c*) Good yields of isoeugenol can also be obtained by fusing eugenol at 210° for eighty minutes with four times its weight of a mixture of sodium hydroxide and potassium hydroxide in the proportions 2 : 1.

3. The addition of liquid paraffin as a diluent does not improve the conversion.

4. Fritze and Co.'s statement that isoeugenol is formed when the potassium salt of eugenol is heated to 190-220° in an indifferent gas has not been confirmed.

5. Autoclaving eugenol with 3 or 4 times its weight of potassium hydroxide in the form of 50 per cent. aqueous solutions gives, on the whole, results similar to those obtained by fusing at 220° with solid potash.

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