synchronization, trials were continued until the image of an explosion was found to be favorably oriented on the film.

### HOUSING OF CAMERAS

To provide adequate protection from the violence of the explosion, the cameras were mounted inside a steel box made from heavy angle iron and $^{3}/_{4}$-inch steel plate. The radiation from the explosion was admitted through a heavy glass window, 3 × 11 inches in size. The interior of the box and the window are shown in Figure 11. The window usually consisted of two thicknesses of standard automobile safety glass. In case there were any fragments of metal or glass from the explosive charge, the outer layer of glass would generally become pitted and eventually crack; it was then replaced. If heavy charges were fired, in close proximity—that is, within 2 feet of the window—the second thickness of safety glass was replaced with $^{1}/_{2}$-inch tempered glass.

The steel box was mounted in a wall of the chamber in which the explosives were fired (Figure 4). Chamber was 8 × 8 × 7 feet in size and had walls and roof of reinforced concrete 2 feet thick. It was vented through a passageway 30 inches wide which wound partly around the outside and had three right-angle turns designed to attenuate the noise of the explosion and prevent daylight from reaching the inner chamber. Its effectiveness was enhanced by lining the passageway with cinder concrete block. Forced ventilation was provided in order to clear rapidly the fumes from an explosion. The chamber has been subjected to considerable use in the past six years and no serious evidence of deterioration is yet apparent.

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# RACEMIC MENTHOL

## NEW SYNTHESIS FROM THYMOL

A new synthesis of racemic menthol from thymol is described, in which the desired products are separated in each of two steps by precision vacuum rectification. The use of a dehydrogenation catalyst in conjunction with a sixty-plate column allows the complete conversion of all the hydrogenation products of thymol to *dl*-menthone, which can then be catalytically reduced to give a good conversion to *dl*-menthol. All by-products obtained may be recycled, and the *dl*-menthol produced is indistinguishable in taste and odor from pure *l*-menthol.

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MENTHOL finds extensive use as a flavor and scent in a large variety of foods and cosmetics, as well as in numerous pharmaceutical preparations. The transportation of the naturally occurring form from its chief sources in the Orient is expensive in peacetime and impossible at present; the desirability of having a domestic source of this valuable chemical is apparent.

The substitution of racemic menthol for the *levo* form found in nature has been repeatedly urged, but the difficulty of preparing *dl*-menthol free from its isomers, all of which have a disagreeable taste and odor, has prevented the replacement of the natural form by the racemic. In spite of numerous contradictory statements in the literature, pure racemic menthol is indistinguishable by the average chemist in taste and odor from recrystallized *l*-menthol. Pharmaceutical differences are slight, if any, so that there seems no reason why *dl*-menthol of a satisfactory purity cannot be substituted for the natural *levo* form in most of the latter's uses.

The ready availability of thymol by the isopropylation of *m*-cresol has made this an attractive potential source of synthetic menthol ever since catalytic hydrogenation has been known. Much work on the problem has been done in the last four dec-

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ades, but the difficulty of separating *dl*-menthol from the complex mixture with its isomers and the ketones related to the four menthols has remained an obstacle. The only satisfactory separation has been achieved by the fractional crystallization of solid esters of the various isomers, followed by regeneration of the alcohol by hydrolysis of the purified ester (*4, 6, 7*).

The process described here involves the separation of *dl*-menthone as an intermediate in the reduction of thymol to menthol, and the reduction of the ketone to the desired product. The separations necessary are carried out by fractionation under vacuum in a column of about sixty-plate efficiency. The high yields and relatively high conversions obtained, and the ease with which the by-products may be recycled, add to the attractiveness of the physical separation used.

PURE *dl*-menthone can be obtained from thymol in practically quantitative yields in a two-step process. Thymol is hydrogenated in any convenient manner to the complex mixture of the alcohols and ketones of the menthol series; their relation to one another and to thymol is indicated in Figure 1. By rectifying this mixture in the presence of a dehydrogenation catalyst and of a catalyst to promote enolization, with a sufficiently efficient column, it is possible to convert the whole mixture practically quantitatively to pure *dl*-menthone. In the course of this process the alcohols are dehydrogenated to the corresponding ketones, and the equilibrium,

$$dl\text{-isomenthone} \rightleftharpoons \text{enol} \rightleftharpoons dl\text{-menthone}$$

is continuously displaced to the right by the removal of *dl*-menthone; eventually the conversion to pure *dl*-menthone is complete. Successful operation depends on the use of a column of approximately sixty-plate efficiency at least; this is the efficiency calculated by the use of Rose's approximation (*5*) relating boiling points and column efficiencies and Huggett's values (*2*) for the physical constants of the two ketones. Attempts to carry out the dehydrogenation-isomerization-rectification with columns of lower efficiency gave less satisfactory results. A typical experiment is described below.

Table I. Effect of Temperature and Pressure on Hydrogenation Products

| Original $H_2$ Pressure, Lb./Sq. In. | Temperature, ° C. | Ketones, % | Alcohols, % | Conversion to Base-Insol. Products, % |
|---|---|---|---|---|
| 600 | 150–160 | 80 | 20 | 65 |
| 800 | 150–160 | 50 | 50 | 70 |
| 1000 | 170–190 | 30 | 70 | 75 |

One hundred grams (110 ml.) of crude hydrogenated thymol (mostly alcohols) were placed in the still pot of the precision column with 10 grams of Adkins' copper chromite catalyst (*1*) and 1 gram of solid sodium hydroxide to promote enolization. The column was packed with a nickel Lecky-Ewell spiral gauze screen (*3*) to a height of 7 feet, and was provided with jackets and heaters to maintain adiabatic conditions. A total condenser with an adjustable partial take-off and heated reflux return was used. After operation at total reflux for about 10 hours to ensure equilibrium in the column, the rectification was carried out at a reflux ratio from 40:1 to 60:1 by intermittent take-off of small samples; under these conditions the column efficiency as determined by the *n*-heptane-methylcyclohexane separation is sixty plates. Ninety-six milliliters of pure *dl*-menthone (boiling point 68° C. at 6 mm., 100 per cent of distillate) were obtained; the remainder of the charge is accounted for by the holdup of the column and losses through the condenser. The pot residue consisted only of the dry catalyst which could be re-used.

The *dl*-menthone produced had a melting point of −16° C., determined by plotting a thawing curve of temperature against time: it analyzed 100 per cent $C_{10}H_{18}O$ by the hydroxylamine hydrochloride–alkali titration, and better than 95 per cent *dl*-menthone by formation and separation of the semicarbazones of it

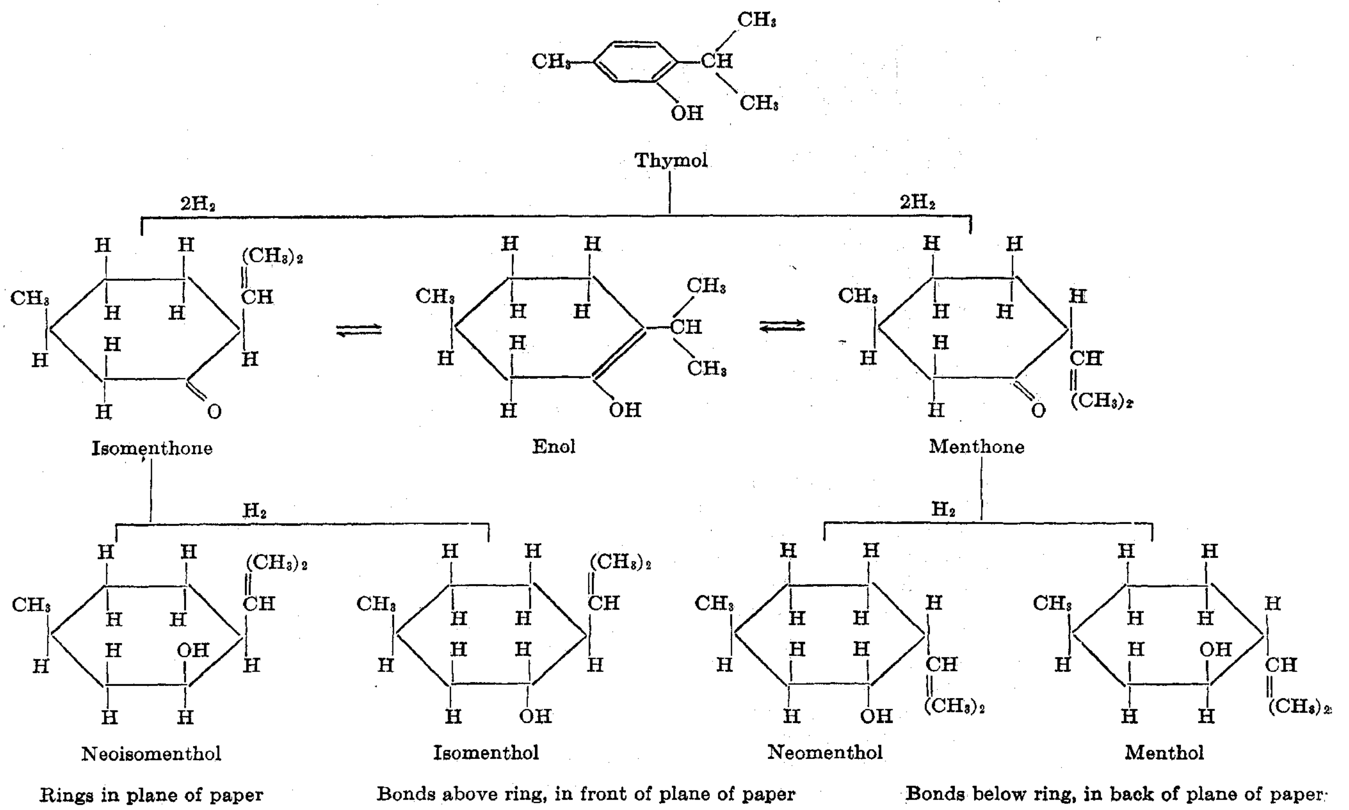

**Figure 1. Stereochemistry in the Menthol Series**

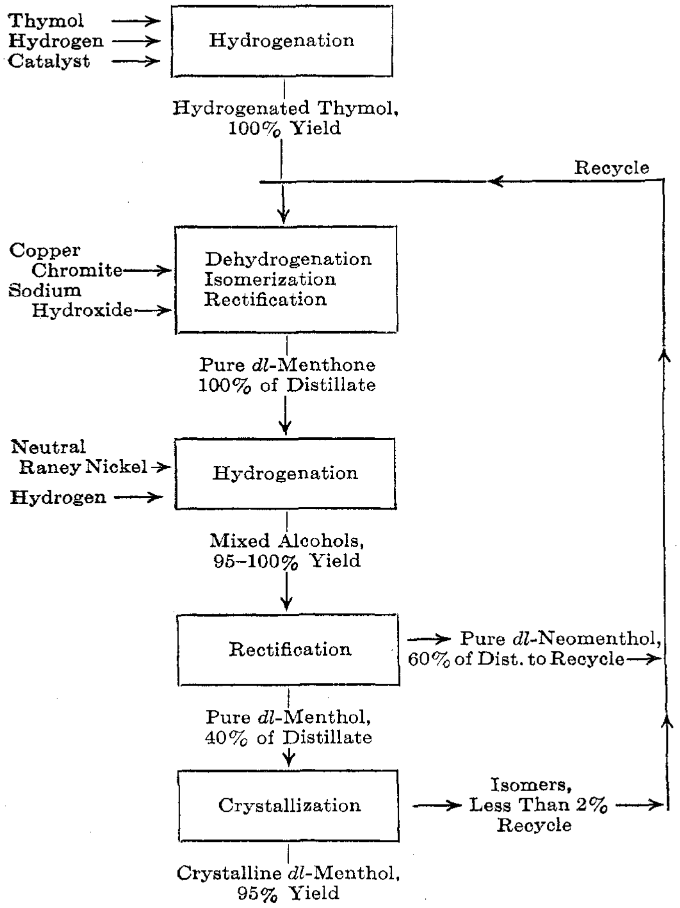

**Figure 2. Flow Sheet for Preparation of Racemic Menthol from Thymol (Yields to Nearest 5 Per Cent)**

and of *dl*-isomenthone, which is close to the limit of accuracy of the latter analysis.

Experiments were carried out with similarly satisfactory results, using Raney nickel as the dehydrogenation catalyst, at pressures as high as 100 mm. corresponding to pot temperatures up to 150° C., with hexahydrothymol from various sources. The presence of unreacted thymol in the charge has a deleterious effect on the copper chromite catalyst, and its substantial removal by one alkali washing is recommended. The use of Raney nickel in some runs led to further dehydrogenation of some of the menthone to thymol, so that the copper catalyst is preferred.

It is desirable to have as much as possible of the hydrogenated thymol at the ketone stage of reduction to minimize the amount of hydrogen given off in the rectification. It is possible to control the reduction to obtain ketones predominantly but the further addition of hydrogen cannot be entirely prevented in any ordinary equipment. By hydrogenation in aqueous alkaline solution, high yields of ketonic material are obtained, but only with relatively low conversion and slow reaction. Attempts to raise the conversion and to accelerate hydrogenation by increasing the temperature and the hydrogen pressure led only to increasing the amount of alcohols produced, as shown in Table I.

THE catalytic reduction of *dl*-menthone to a product from which *dl*-menthol can be readily isolated depends on the use of an active yet neutral catalyst. The presence of acid or alkali catalyzes the inversion of part of the *dl*-menthone to *dl*-isomenthone through their common enol form (Figure 1), and hence gives a mixture of the four alcohols related to the two ketones, similar to the mixture obtained directly from thymol. An alkali-free Raney nickel was found to be satisfactory. A typical experiment follows:

A mixture of 62 grams of pure *dl*-menthone (melting point, −16° C.) and 5 grams of wet Raney nickel catalyst, from which the last traces of alkali had been removed by washing with dilute acetic acid before the final distilled water and alcohol washes, was placed in the hydrogenation bomb. Hydrogen was admitted to a pressure of 900 pounds per square inch. The reduction was carried out at 135° C. with constant agitation and was complete in one hour. Fifty-nine grams of reduction product, having the typical camphoraceous odor of *dl*-neomenthol, were obtained and analyzed by rectification in the sixty-plate column. Two well defined fractions were obtained; the first at a 50:1 reflux ratio, the second, after the column went dry between cuts, at a 1:1 ratio:

| Fraction No. | Yield, Ml. | M. P., ° C. | Product |
|---|---|---|---|
| 1 | 0–30 | 50–51 | *dl*-Neomenthol |
| 2 | 30–49 | 32–36 | *dl*-Menthol |

Both the holdup of the column and the excessively high losses through the condensers, which plugged with crystals of *dl*-menthol if kept cold, make the yield based on the figures shown (30 per cent of the charge, 38 per cent of the distillate) much lower than would be the case in runs on a larger scale; it is probable that the reduction gives about 50 per cent of the desired product.

Copper chromite and Raney nickel as normally prepared give ready reduction accompanied by inversion. The use of metallic sodium and moist organic solvent for the reduction gives preferential reduction to *dl*-menthol, accompanied by some inversion and by some bimolecular reduction. The difficulties involved in the isolation of pure *dl*-menthol from this mixture and the loss of 3 to 10 per cent of the *dl*-menthone, depending on the size of the pieces of sodium used, in forming a bimolecular reduction product make the catalytic reduction preferred even though the yield is slightly lower than that from the active metal reduction (about 50 per cent).

Final purification of the *dl*-menthol obtained from rectification is carried out by crystallization from the melt or from a suitable solvent, such as petroleum ether or methanol. No single criterion is adequate to measure the purity of the final product; the melting point, about 36° C., is not markedly affected by traces of the isomers and is dependent on the rate of heating. The material will liquefy on prolonged standing at 30° C., due to ease of interconversion of at least two crystalline forms.

The by-product, neomenthol, may readily be recycled by adding it to the hydrogenated thymol for the first rectification, or may find its own uses. The over-all process, with yields to the nearest 5 per cent, is shown in Figure 2.

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