Prototocatechualdehyde methylenation. Photo-essay.

What follows is a slight variation of the commonly referenced catechol methylenation procedure, easily found copied and pasted all over the internet. This variation would theoretically produce heliotropin (used in perfumery).
I couldn't find any experimental data to confirm whether this synthesis actually works or not. So lets find out.

Chemicals used:
138g protocatechualdehyde
120 ml 50% NaOH aqueous solution (91g NaOH, 91g dH2O)
500 ml dimethylsulfoxide (DMSO)
120ml (160g) dichloromethane (DCM).

Equipment used:
1L RBF & condenser (for methylenation), stirrer hotplate with oil bath
500 ml RBF (for addition mixture), stirrer mantle
500 ml mixing beaker
3L RBF & heater for steam distillation
Suitable large container for collecting distillate (I used 2L beaker)
Converted steam cooker & aquarium tubing for steam distillation (with short glass tube & cork)
Funnel/cork/glass tubing for reactant addition (though not essential)
1 L separating funnel (for dichloromethane extractions of steam distillate)

No inert atmosphere was used for this experiment.

300 ml of DMSO is added to the 1L RBF, then 120ml dichloromethane is added. Reflux condenser added with cooling water flowing, oil bath heated to 125-130 deg C.

Whilst the bath is heating, the addition mixture is prepared. 120 ml 50% NaOH, 138 g protocatechualdehyde and 200 ml DMSO are combined in a 500 ml beaker (with stir bar), there is some heat evolution and the mixture is stirred on the hot plate for a few minutes to fully dissolve the protocatechualdehyde and any residual NaOH. Once dissolved, the mixture is poured into the 500 ml RBF (rinsed down the funnel with a little extra DMSO), and then transferred to the 500 ml stirrer mantle for heating and stirring. Mixture was kept hot but without boiling. No temperature measurement was used for the addition mixture.

Methylenation solution on left, addition mixture on right.

Once the DMSO/DCM mixture was nicely refluxing (oil bath at round 125 deg C), 15 more minutes were allowed for the addition mixture to stir before addition was started.

Orange addition funnel was connected to a small glass tube, this makes addition much easier, much easier than addition via the condenser.
The drop of addition liquid held in position by capillary force, prevents DCM vapor from exiting the funnel - this works quite well and I can contend this is far easier than using an eyedropper (pipettes tend to melt at this temp), which is very impractical on this scale.

Addition commenced (with vigorous magnetic stirring)

Wearing a rubber glove for heat protection, the hot 500 ml RBF was literally poured into the small addition funnel. A few minutes were allowed in between funnel additions.
This waiting time is necessary because the reaction causes DCM to boil vigorously, it could easily overwhelm the condenser if the additions are not spaced apart (also, according to literature sources, reactant dilution is necessary to improve yields).
In total about 40 minutes were required to complete the addition. The reaction (with vigorous stirring and good reflux) was continued for another 90 minutes, before turning the heat off and allowing to cool (with stirring).

Once cool, the mixture was transferred to a larger container suitable for steam distillation. I had a 3L RBF at hand, so used that. About half a litre of water was added prior to steam distilling.

3L RBF has been set up for distillation (using double surface condenser for good rate of steam condensation), and brought to boiling temperature, and now steam is being added via a small glass tube that is submerged nearly to the bottom of the RBF (though only partly visible in the photo below).

Steam distillate, distilling over quite rich in reaction product:

About 2 gallons of water were put through the reaction mixture (using a pressure cooker as steam source) and condensed.

Once cooled, much of the product crystallizes in the water, and is easily removed by filtration. The

Heliotropin laden water is kept for solvent extraction later. It still contains a few grams per Liter.

Glass sintered filter funnel (after filtering a small amount of cooled steam distillate).

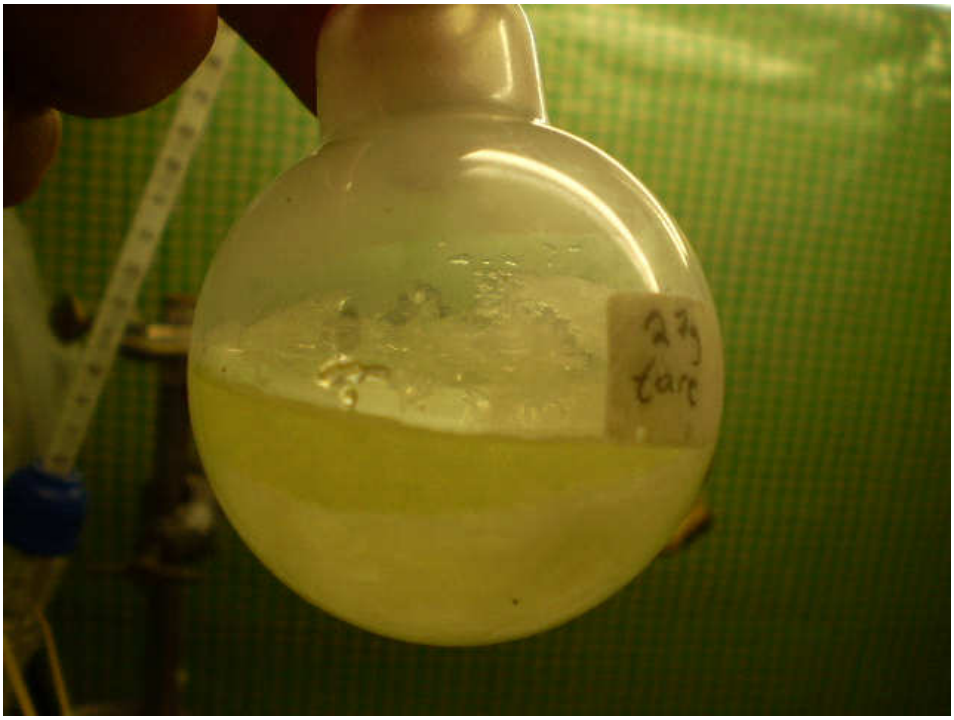
2L beaker

Filtering the product

The total dried crystals yield was around 34 grams.
The filtered water was extracted with about 30 ml DCM per litre.

The combined DCM extracts were combined, and added to a 500 ml RBF for distillation (using the large double surface condenser).
Once the DCM was mostly distilled off, the condenser was changed for a small liebig condenser, and set up for vacuum distillation.
I was expecting multiple fractions, however the still head (under full vacuum) rapidly rose to 140 deg C and slowly rose to 143 by the end of the distillation. So I only ended up collecting one single fraction,

Product rapidly crystallising in receiver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Product crystallising in the condenser

Vacuum distillation yielded 26 grams, far more than i was expecting. There was some product still in the steam distilled water when it was discarded (as it still had a strong smell of vanilla/piperonal). If I'd known it held up so much product, I'd have carried out at least 3 x 30 ml DCM extractions per liter.

Also, I stopped the steam distillation when the distillate stopped appearing milky/turbid. However, the last liter, although not milky in appearance, still produced lots of crystals, so I feel I stopped the steam distillation too soon.

The total combined yield was 60 grams, of a product which appears indiscernible (in terms of color, taste, smell, texture and melting point) to another small sample of heliotropin that I've compared it with. Assuming this product is pure heliotropin/piperonal, then this equates to an overall molar yield of 40 %. Not too bad, but clearly there is still room for improvement.