EXPERIMENT 8: ISOLATION OF THE ESSENTIAL OILS OF SPEARMINT AND CARAWAY: (−)- AND (+)-CARVONE

AN INTRODUCTION TO STEAM DISTILLATION AND THE PROPERTIES OF ENANTIOMERS.
(S)-(+-)-CARVONE AND (R)-(–)-CARVONE

(S)-(+-)-CARVONE
CARAWAY SEEDS

(R)-(–)-CARVONE
SPEARMINT LEAVES
STEAM DISTILLATION: ESSENTIALS

SET-UP FOR SPEARMINT LEAVES

REDUCING ADAPTER

500mL R.B.

LARGE HEATING MANTLE

SET POWERMITE TO ~ 7 UNITS
ISOLATION OF (−)- AND (+)‐CARVONE FROM CARAWAY AND SPEARMINT: THE OPTIONS

- SIMPLY TAKE THE PLANT MATERIAL AND PRESS THE CARVONE OIL OUT.

- EXTRACT THE OIL USING AN ORGANIC SOLVENT SUCH AS DICHLOROMETHANE (CH₂Cl₂).

- EXTRACT THE OIL USING STEAM DISTILLATION.

  STEAM DISTILLATION IS THE CO‐DISTILLATION OF A MIXTURE OF WATER (STEAM) AND AN ORGANIC COMPOUND

- IT IS MUCH MORE SELECTIVE THAN PRESSING THE PLANT MATERIAL OR EXTRACTION USING AN ORGANIC SOLVENT.
STEAM DISTILLATION: THEORY

- The organic compound must be insoluble (immiscible) in water for the steam distillation to be successful.

- Immiscible mixtures such as water and an organic compound do not behave like solutions.

- For a mixture of immiscible liquids:

  \[ P_{\text{total}} = P_{\text{water}} + P_{\text{carvone}} \]

- The total vapour pressure does not depend on the amount of each compound that is present.
STEAM DISTILLATION: THEORY

- BOILING OCCURS WHEN THE MIXTURE OF WATER AND CARVONE HAS A VAPOUR PRESSURE EQUAL TO THE EXTERNAL (ATMOSPHERIC) PRESSURE:

\[ P_{\text{TOTAL}} = P_{\text{ATMOSPHERIC}} \]

SINCE:

\[ P_{\text{TOTAL}} = P_{\text{WATER}} + P_{\text{CARVONE}} \]

STEAM DISTILLATION: THEORY

- B.P.\textsubscript{WATER} = 100°C
- B.P.\textsubscript{CARVONE} = 230°C
- B.P.\textsubscript{WATER + CARVONE} < 100°C

- STEAM SELECTIVELY ISOLATES THE CARVONE FROM THE SPEARMINT OR CARAWAY PLANT MATERIAL.

- THE CARVONE CO-DISTILLS WITH THE STEAM AT A TEMPERATURE FAR BELOW ITS BOILING POINT IN PURE FORM.
**COMPOSITION OF THE VAPOUR**

\[
\frac{\text{moles of water}}{\text{moles of carvone}} = \frac{P_{\text{WATER}}}{P_{\text{CARVONE}}}
\]

LOWER B.P. ⇒ HIGHER VAPOUR PRESSURE, P  
HIGHER B.P. ⇒ LOWER VAPOUR PRESSURE, P

⇒ A LARGE VOLUME OF WATER DISTILS WITH A SMALL VOLUME OF CARVONE. DISTILLATION IS CONTINUED UNTIL THE SUPPLY OF THE ORGANIC COMPOUND IS EXHAUSTED.
CONTENTS OF THE RECEIVING TUBE

- CARVONE AND WATER CO-DISTIL, BUT ARE IMMISCIBLE WITH ONE ANOTHER.

- UPON ENTERING THE RECEIVING TUBE THE LIQUIDS SEPARATE TO GIVE TWO DISTINCT LAYERS.

- CARVONE IS LESS DENSE THAN WATER, SO FORMS THE UPPER LAYER.

- CARVONE HAS LIMITED SOLUBILITY IN WATER; THIS WILL BE EXPLOITED BY CARRYING OUT CHEMICAL TESTS ON THE AQUEOUS DISTILLATE (TESTING FOR C=\text{C} \Rightarrow \text{CARVONE PRESENT}).
CHEMICAL TESTS FOR THE PRESENCE OF A CARBON-CARBON DOUBLE BOND: PREPARATION

- As the distillate collects in the receiving tube, periodically drain the lower aqueous layer. This will allow you to conduct the chemical tests while the distillation runs to completion.

- The KMnO₄ test can be performed directly on the aqueous distillate.

- Since Br₂ reacts with water, this test must be performed in an inert solvent. The carvone will therefore be extracted from the aqueous distillate into hexane using liquid-liquid extraction. The hexane extract will then be used for the chemical test.
CHEMICAL TESTS FOR THE PRESENCE OF A CARBON-CARBON DOUBLE BOND: KMnO₄

KMnO₄ OXIDISES C=C TO GIVE VICINAL DIOLS.

A CHANGE FROM A DEEP PURPLE SOLUTION TO A CLEAR SOLUTION CONTAINING A BROWN PRECIPITATE IS A POSITIVE TEST FOR THE PRESENCE OF C=C.
CHEMICAL TESTS FOR THE PRESENCE OF A CARBON-CARBON DOUBLE BOND: Br$_2$

Br$_2$ ADDS TO C=C TO GIVE VICINAL DIBROMIDES. SINCE Br$_2$ ALSO UNDERGOES A LIGHT-INITIATED REACTION WITH ALKANES, THIS TEST MUST BE PERFORMED IN THE DARK.

A COLOUR CHANGE FROM ORANGE/BROWN TO CLEAR AND COLOURLESS IS A POSITIVE TEST FOR THE PRESENCE OF C=C.
DRAIN ALL OF THE REMAINING AQUEOUS DISTILLATE FROM THE RECEIVING TUBE. DISCONNECT THE RECEIVING TUBE AND TRANSFER THE OIL TO A 25mL ERLENMEYER USING A LONG PASTEUR PIPETTE.
CHARACTERISING THE OIL

- DRY THE OIL OVER Na₂SO₄ AND THEN TRANSFER TO A LABELLED, PRE-WEIGHED VIAL.

- ALLOW HEXANE TO EVAPORATE FROM THE VIAL.

- RECORD THE IR SPECTRUM OF YOUR OIL (IR SPECTRA FOR BOTH CARVONE ENANTIOMERS ARE PROVIDED FOR REFERENCE).

- NOTE AND COMPARE THE DISTINCT ODOURS OF THE TWO CARVONE ENANTIOMERS.
COMPLETING EXPERIMENT 8

- HAND IN THE ISOLATED CARVONE.

- A LAB REPORT IS REQUIRED FOR EXPERIMENT 8.

- HAND IN YOUR IR SPECTRUM WITH THE LAB REPORT. REMEMBER TO FULLY INTERPRET THE SPECTRUM.