

CHAPTER III

EXPERIMENTAL

Instruments and Apparatus.

1. Hydrogenator.

Parr Instrument Company. model 4551 Pressure reactor with 4842 Automatic temperature controller.

2. Fourier-Transform NMR Spectrometer.

The NMR model AC-F 200 (200 MHz) From Bruker.

3. Gas Chromatograph-Mass Spectrometer (GC-MS).

The apparatus model GC 8000 series and Mass Spectrometer model MD 800 from Fison Instrument.

4. GC-MS Condition.

Column : DB-1 capillary column 30m×0.25mmID×0.25μm.

Carrier : Helium 50cm/sec.

Oven : 100(3) to 180°C rate 15°C/min., 180 to 250°C (10) rate 10°C/min.

Injection temperature : 250°C

Detector : MS (EI⁺ 70eV)

5. High Vacuum Pump.

Edwards, model E2m2 20035. 7

Materials.

1. Rosin was supplied from commercial available in Bangkok.
2. Diethyl Ether was reagent grade and available from J.T. Baker Inc..
3. Hydrogen Gas (Purity 99.50% minimum) was industrial grade and was available from TIG Trading Limited.
4. Potassium Hydroxide was reagent grade and available from Fluka, Switzerland
5. N-methyl-N'-nitro-N-nitrosoguanidine was reagent grade and available from Fluka, Switzerland.
6. Raney Nickel Catalyst (with about 50% water) was available from Merck.
7. Platinum on Alumina Support was supplied from United Catalyst Inc.
8. Palladium on Activated Charcoal, containing 5% by weight of Palladium and 50% by weight of water was available from Fluka, Switzerland.
9. Miscellaneous solvents were distilled before using.

Experiment Based on Methylation. [24,25]

N-methyl-N'-nitro-N-nitrosoguanidine (about 70 mg) was dissolved in 5 ml of ether. The solution was placed in a 50 ml distillation flask equipped with a dropping funnel in which was contained 0.5 ml of 40% KOH and a double surface condenser that was cooled by circulating cold water. The receiving flask (50 ml) which contained the ethereal solution of sample (30 mg). Distilling flask and receiving flask were cooled in an ice bath. The solution of KOH in the dropping funnel was added dropwise to the distilling flask and the diazomethane was generated in the ether solution.

After about 5 minutes, the ethereal solution of diazomethane was heated on a water bath and the solution was condensed downward to the receiving flask containing the ethereal solution of the sample incorporating with a magnetic stirring unit. The esterification reaction was complete when bubbles were no longer visible and the yellow color of the solution disappeared. The solution of esterified sample was transferred to a volumetric flask (50 ml) and the volume was adjusted to 50 ml with diethyl ether, and stored at 4°C for GC-MS analysis.

Raw Material Analyses.

Rosin (commercial grade) was esterified with excess diazomethane as described in experiment C and the result was analyzed by GC-MS to determine resin acid composition.

The peak area of each peak from chromatogram of resin acids was calculated to obtain the percentage composition of resin acids. The structure of each component was determined from a library search program supported on the GC-MS.

The GC-MS chromatogram of the original rosin is displayed in Figure A1. The percentage composition of resin acids is presented in Table 4.1 and Figure 4.1.

Experiments Based on Dehydrogenation (Disproportionation Reaction)

[15,16,21]

Unpurified gum rosin (100 g) and palladium⁷ on charcoal (0.3 g) were placed in a stainless steel reactor. Gas in the reactor was replaced by nitrogen

gas. The reaction was operated at various temperatures (240, 260 and 280°C) in separate experiments with stirring for 4 hours. After that the mixture was cooled to room temperature. Then the pressure in the reactor was released and the product in the reactor was added to 200 ml of acetone with stirring until the rosin was dissolved homogeneously in acetone. The solution was poured into the 500 ml beaker removing the catalyst by filtration. Acetone was removed by distillation to give disproportionated rosin residue. This residue was distilled under pressure of 3 mmHg in an atmosphere of nitrogen to give a purified rosin as the main fraction. The results are shown in Table 4.4.

1. Characterization and Quantitative Analysis.

Dehydrogenated rosin (disproportionated rosin) was esterified with excess diazomethane as described in experiment C and was analyzed by GC–MS. Percentage compositions of dehydrogenated rosins were calculated from the peak areas. The structure of each component was determined by GC–MS with the library search program.

The GC–MS chromatograms of dehydrogenated rosin at various temperatures is shown in Figure A 9. The percentage yields of dehydrogenation of rosin are presented in Table 4.5 and Figure 4.2. Mass spectra of each peak in dehydrogenated rosins are presented in Figure A 10.



Experiments Based on Hydrogenation.

1. The Effect of Catalyst on the Hydrogenation. [2, 14, 15]

Unpurified rosin (200 g), Raney Nickel (4%, with about 50% water), and ethanol (300 ml) were placed in a stainless steel reactor. The gas in the

reactor was replaced by hydrogen gas by successive dilution and the hydrogen pressure in the reactor was adjusted to 500 psi. The reaction was operated at the selected temperature (200°C) and reaction time (6 hours), with constant stirring. The mixture was cooled to room temperature, the pressure was released, the content was transferred to 1 liter beaker, and the catalyst was separated by filtration to obtain hydrogenated rosin.

The hydrogenated rosin was esterified with diazomethane as described in D and was analyzed by GC-MS. The percentage yield of hydrogenation products were determined by calculation of peak areas. The mass spectra obtained were characterized by the library search program support on the GC-MS.

Additional hydrogenation experiments were conducted following a procedure similar to that described above except various types of catalyst (Pt/Al₂O₃, Pd/C, Pt/C) were used. After the reaction took place the reaction mixtures were worked up in the same manner to give the desired products. These hydrogenated rosins were analyzed in the same manner as above.

The GC-MS chromatograms of these hydrogenated rosins are shown in Figure A 11. The percent yields and the effect of catalyst type of hydrogenated rosins are presented in the Table 4.6. Mass spectra of each peak were presented in Figure A 12.

2. The Effect of Reaction Temperature on Hydrogenation.

Following the same procedure in experiment 1 except the reaction was operated at various temperatures (room temperature, 100, 150 and 200°C) and the most suitable catalyst obtained from experiment 1 was used. After the reaction was completed, the mixture was worked up in the same manner to give

desired products. The percentages of hydrogenation products were determined as described in experiment 1.

The GC–MS chromatograms of hydrogenated rosin produced at various temperatures are shown in Figure A 13. The percentage yields of hydrogenated rosins were presented in Table 4.7. The effect of reaction temperature on percentage yield of hydrogenated rosins is shown in Figure 4.3. Mass spectra of each peak in the hydrogenated rosin produced at various temperatures are shown in Figure A 14.

3 The Effect of Reaction Times on Hydrogenation.

Following a procedure similar to that described in experiment 2 except various reaction times (8, 10, 12, and 16 hours) at the optimum temperature from procedure 2 were used. After the reaction was completed, the mixture was worked up in the same manner to give the desired products. The percentage yields of hydrogenated rosins were determined as described in experiment 1.

The GC–MS chromatograms of hydrogenated rosin produced during various reaction times are shown in Figure A 15. The percentage yields of hydrogenated rosin were presented in the Table 4.8 and Figure 4.4. The mass spectra of each peak in the hydrogenated rosin produced during the various reaction times are displayed in Figure A 16.

4 The Effect of Hydrogen Pressure on Hydrogenation

Following the same procedure described in experiment 3 except the reaction was operated at various hydrogen pressures (500, 600 and 700 Psi) for the optimum reaction time obtained from experiment 3. After the reaction was

completed, the mixture was worked up in the same manner to give the desired products. The percentages of hydrogenated rosins were determined as described in experiment 1.

The GC–MS chromatograms of hydrogenated rosin produced at various hydrogen pressures are shown in Figure A 17. The percentage yields of hydrogenated rosins are presented in Table 4.9. The effect of hydrogen pressures on hydrogenated rosin were shown in Figure 4.5. Mass spectra of each peak in hydrogenated rosin produced at the various hydrogen pressures are presented in Figure A 18.

5 The Effect of Catalyst Concentration on Hydrogenation.

Following the same procedure as described in experiment 4 except the reaction was operated at various catalyst concentrations (8, 10, and 12%) using the optimum hydrogen pressure obtained from experiment 4. After the reaction was completed, the mixture was worked up in the same manner to give the desired products. The percentage yields of hydrogenated rosins were determined as described in experiment 1.

The GC–MS chromatograms of hydrogenated rosin produced at various catalyst concentrations are shown in Figure A 19. The percentage yields of hydrogenation of rosin were presented in the Table 4.10. The percentage yields of hydrogenated rosins are shown in Figure 4.6. Mass spectra of each peak in the hydrogenated rosin produced at the various catalyst concentration are shown in Figure A 20.