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Comparative Study of Yields of Heptaldehyde and Undecylenic Acid from Castor Oil and Its Derivative

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ABSTRACT

Heptaldehyde and Undecylenic acid are two important by products of castor oil and their use in the industry is immense. They are derived from Castor oil. The present study compares the yields of these two compounds from castor oil and the methyl ester of castor oil. Different parameters like temperature, acid treatment, alkali treatment, temperature and presence of excess reactants were studied. Methyl Ester of castor oil produced better yields of both these compounds as compared to castor oil. The percent increase in yields of Heptlaldehyde and Undecylenic acid were 17.0371 and 13.494 at 1hour and 8.08 and 10.204 for 2 hours of incubation for castor oil and methylated ester of castor oil, respectively.

Keywords: Heptaldehyde, Undecylenic Acid, Methyl ester, Castor oil.

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INTRODUCTION

Castor oil is non- edible oil obtained from castor seeds. Castor plant, *Ricinus communis* belonging to family, Europhobiaceae. India and China account for 50% of global castor oil production. The area under cultivation of Castor in India is about 5, 00, 000 acres and Andhra Pradesh accounts for 73% of this area. Castor oil is extracted for the seeds of castor either by local conventional methods or industrially in large quantities. Thus castor oil is available in plenty in our country. Many castor oil derivatives with lot of potential industrial use are not being manufactured in our country and they are being imported. These derivatives are used for surface coating materials, textile auxiliaries, perfumery chemicals, polymeric compounds and surfactants. Thus there is plenty of scope for developing indigenous methods for the production of such derivatives in large scale due to the availability of castor seeds in the country. This will not help easy availability of these derivatives in the local market it can also reduce the import burden on the exchequer.

The derivatives can also tap export potential to earn foreign exchange for the country. There are two important derivatives of castor oil, namely, Heptaldehyde and Undecylenic acid, which are produced by standard techniques. Heptaldehyde, which is by product of pyrolysis of castor oil, is used in perfumery industry since it has a natural fruity flavour. Heptaldehyde is a colourless liquid, oily, fruity odour, penetrating, hygroscopic, soluble in water, ether and combustible. This is oxidized to yield a hepatonic acid and by reducing it produces heptyl alcohol, which combine to form heptyl heptanes, a perfume which combines well with Coumarins. Hapatonic acid esters have variety of fruity flavours. [4] Aldol condensation of heptaldehyde with bezakdehide yields amyl cinnamic aldehyde which is an important perfume. [1]

Undecylenic acid as well as its zinc salt, are used as bactericidal, fungicidal and also used for diseases like athlete foot. Derivatives of this acid have extensive perfumery outlets. This alcohol has an intense penetrating odour and the saturated 11 carbon aldehyde is used in the modification of floral odours. Treatment of this acid with strong sulphuric acid gives gamma-Undecalcetone which is also called peach aldehyde. [1]

A volume outlet for Undecylenic acid lies in the preparation of nylon 11, 11. Hydrobromination of the acid in presence of peroxide catalysts yields the terminal bromide which on heating melts and then condenses in head to tail fashion to yield a 11,11- polyamide called Rilsan having melting point of about 188 ^{0}C. It is a colourless to pale yellow liquid with a waxy and creamy constitution having molecular weight of 184.28 grams.

The present study aims at comparing the percent yields of production of Heptaldehyde and Undecylenic acid from castor oil and from the methyl ester of castor oil [2, 3]. It was observed that the methylated castor oil gave better yields for both these compounds. Wit is suggested that instead of using castor oil for the manufacture of these compounds we can use the methylated ester of castor oil.

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MATERIALS AND METHODS

Among the different methods that in available like pyrolysis of castor oil in glass assembly, pyrolysis in the presence of inert medium, pyrolysis in packed glass assembly, pyrolysis in unpacked cylindrical reaction vessels and pyrolysis in packed tubular reactor etc. we have chosen pyrolysis in glass assembly method due to following advantages.

i. The method is simple and can be easily carried out.
ii. The effect of initiators is insignificant.
iii. There is no need of inert materials, and
iv. The yields are high.

The procedure was divided into four steps.

A. Acid catalysed methanolysis of castor oil was used since the process was simple and catalyst was easily available.
B. Alkali catalysed methanolysis was used because the methanolysis percent was high there is no soap formation and preparation of sodium methoxide was simple.
C. Preparation of Heptaldehyde and Undecylenic Acid
D. Analysis and estimation of the products, viz. glycerol, heptaldehyde and Undecylenic acid.

Acid Catalysed Methanolysis

The method of was followed. 50 gm. of castor oil was taken in a double necked flask and methanol was added along with conc. H_2SO_4/ Conc. HCl as catalyst. The reaction mixture was kept in a magnetic stirrer with air reflux for lower temperature reaction. For higher temperature experiment water reflux was used. The mixture was than distilled to separate the unreacted methanol. The product mixture was separated in to glycerol and methyl ester by using separated by using separating funnel. Water wash was allowed during separation. The glycerol from the washing was collected and analysed. The methyl esters were dried. [5]

Alkali Catalysed Methanolysis

The method of was followed. Castor oil was taken in a double necked flask and methanol was added along with freshly prepared methoxide as a catalyst. The reaction mixture was kept in a magnetic stirrer with air reflux for lower temperature reaction and in water reflux for higher temperature reaction. The mixture was distilled to separate the unreacted methanol. The product mixture was separated in to glycerol and methyl ester in separating funnel. Water was allowed during the process. The glycerol from the water wash was collected and analysed. The methyl ester was dried. [6]

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Pyrolytic Decomposition

Castor oil/ Methyl esters were taken separately in three necked flask. The temperature of the system was maintained at 340-360 ^{0} C under vacuum to allow Pyrolytic decomposition. The product heptaldehyde and undecylenic acid/methyl undecylenate were condensed and collected as top layer products.

The heptaldehyde and Undecylenic acid were separated by distillation due to their different boiling points.

Analysis of the Products

Analysis of Glycerol

i. It is completely miscible in water.
ii. On strong heating with sodium bisulphate is gave irritating odour due to the formation of acrolein.
iii. 1 ml of test solution was added with 1 ml of phenol and boiled for 120 ^{0} C. after cooling 1 ml of ammonium hydroxide was added which formed pink colour indication presence of glycerol.

Estimation of Glycerol

This was as per the method of Cocks and Van Rede, 1966 [7].

i. 5 gms of sample was taken in a conical flask and 100 ml of distilled water and 6 drops of phenol red indictor was added to it. Few drops of 5% H_2 SO_4 were added to this to retain yellow colour. This solution was boiled for 2 min and allowed to cool. The solution was neutralised with 0.1 N NaOH solutions. 50 ml of sodium periodate was added to it, shaken well and kept for 30 min in dark. Then the solution was titrated against 02.N NaOH to find the quantity of glycerol present. The same procedure was followed for blank sample simultaneously.

Analysis of Heptaldehyde

Reduction of Fehling's Solution

1ml of sample solution was added to 1 ml Fehling's solution and the formation of red precipitate indicated the presence of aldehyde.

Schiff's reagent Test

To 1 ml of test sample 1 ml of Schiff's reagent was added along with 1 ml of distilled water. The formation of purple red colour precipitate indicated the presence of aldehyde.

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Analysis of Undecylenic Acid

Ester test

A small quantity of test solution was taken in a test tube and mixed with excess amount of alcohol. The mixture was boiled after adding 2 drops of conc.H_2 SO_4 as catalyst. This mixture was immediately poured into a beaker with cold water. A fruity smell of ester was observed indicating the present of ester bond in the sample.

Carboxylic Group Test

A small quantity of test solution was added with sodium bicarbonate in a test tube resulting in the release of CO_2 as effervescences, indicating the presence of carboxylic group in the test sample.

RESULTS AND DISCUSSION

The results were divided into 4 sub headings where the different parameters for conversion were observed.

Acid catalysed methanolysis
Alkali Catalysed methanolysis
Parameters controlling percent yield of Heptaldehyde and Undecylenic acid

Acid Catalysed Methanolysis

Effects of Parameters

Experiments were conducted to obtain glycerol and methyl esters by methanolysis of castor oil and the following parameters on percentage conversion of castor oil was studied as

% Conversion = (Glycerol liberated/Actual Glycerol content) x 100.

Effect of Reaction Time

It was observed that the percent conversion of castor oil increased with reaction time and the optimum reaction duration was found to be four hours, beyond which the conversion slowed down. The results were almost similar when 5% H2sO4 and 5% HCl were used separately. (Table1, 2)

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Table 1: Effect of Reaction Duration on percentage Conversion at Temperature 29 ^{0} C and with catalyst 5% Conc. H_2SO_4.

S.No.	Reaction Duration (Hr.)	Wt. of Castor Oil (gms)	Wt. of methanol(gms)	Catalyst Used(ml)	Amount of Glycerol liberated(gms)	% Concersion of Glycerol
1	½	40	40	2	2.118	53.66
2	1	40	40	2	2.786	65.3
3	2	40	40	2	2.876	72.82
4	3	40	40	2	3.104	76.213
5	4	40	40	2	3.444	87.2
6	5	40	40	2	3.46	87.8

Table 2: Effect of Reaction Duration on percentage Conversion at Temperature 29 ^{0} C and with catalyst 5% Conc. HCl.

S.No.	Reaction Duration (Hr.)	Wt. of Castor Oil (gms)	Wt. of methanol(gms)	Catalyst Used(ml)	Amount of Glycerol liberated(gms)	% Concersion of Glycerol
1	½	40	40	2	1.84	46.66
2	1	40	40	2	2.38	60.28
3	2	40	40	2	2.74	69.74
4	3	40	40	2	3.104	74.23
5	4	40	40	2	3.41	86.4
6	5	40	40	2	3.44	87.10

Effect of Temperature

It was observed that up to 60 ^{0} C the conversion of castor oil to was increasing and beyond which it started decreasing as the solubility of glycerol increases as temperature raised. Thus the optimum temperature was maintained at 60^0 C. The results were similar when 5% H^2SO^4 and 5% HCl were used separately (Table 3, 4).

Table 3: Effect of reaction Temperature on Percentage Conversion with 5% Con. HCl as catalyst and at duration of 4 Hrs

S.No.	Reaction Temperature (^{0} C)	Wt. of castor oil(gms)	Wt of methanol (gms)	Catalyst (ml)	Amount of glycerol Liberated(gms)	% Conversion Of Glycerol
1	29	40	40	2	3.446	87.26
2	40	40	40	2	3.494	88.472
3	50	40	40	2	3.512	88.92
4	60	40	40	2	3.568	90.34
5	70	40	40	2	2.912	73.84

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Table 4: Effect of reaction Temperature on Percentage Conversion with 5% Con. H_2SO_4 as catalyst and at duration of 4 Hrs.

S.No.	Reaction Temperature (^{0} C)	Wt. of castor oil (gms)	Wt of methanol (gms)	Catalyst (ml)	Amount of glycerol Liberated (gms)	% Conversion Of Glycerol
1	29	40	40	2	3.412	86.4
2	40	40	40	2	3.44	87.2
3	50	40	40	2	3.468	87.8
4	60	40	40	2	3.499	88.6
5	70	40	40	2	2.89	73.21

Alkali Catalysed Methanolysis

The following parameters were taken into consideration.

Effect of Reaction Duration.

From the experimental data it is clear that the percentage conversion of castor oil was optimum at 2 hours and after 4 hours the reaction rate slowed down. (Table 5)

Table 5: Effect of reaction Duration on Percentage Conversion with Sodium methoxide as catalyst and at Temperature 30 ^{0} C.

S.No.	Reaction Duration (Min)	Wt of castor Oil(Gms)	Wt. of Methanol (gms)	Amount of Glycerol Liberated (gms)	% conversion of Glycerol
1	30	40	16	2.945	74.6
2	60	40	16	3.189	80.8
3	90	40	16	3.329	84.34
4	120	40	16	3.470	87.9
5	150	40	16	3.482	88.2

Effect of Temperature

It was found that up to 60 ^{0} C there was an increase in the conversion rate after which it decreased considerably. (Table 6)

Table 6: Effect of reaction Temperature on Percentage Conversion with Sodium methoxide as catalyst and at 2 hrs Duration

S.No.	Reaction Temperature (^{o}C)	Wt of castor Oil (Gms)	Wt. of Methanol (gms)	Amount of Glycerol Liberated (gms)	% conversion of Glycerol
1	30	40	16	3.47	87.9
2	40	40	16	3.502	88.72
3	50	40	16	3.578	90.63
4	60	40	16	3.647	92.4
5	70	40	16	3.329	84.34

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Effect of Excess Reactant

There was a steady increase in conversion till the methanol was used up to 50% at which the reaction went up to 92.8%. Thus the optimum amount of methanol was fixed at 40%. (Table 7)

Table 7: Effect of Excess reactant on Percentage Conversion with Sodium methoxide as catalyst and at 60 ^{0} C.

S.No	Wt. of Castor Oil (gms)	Wt % 0f Methanol(gms)	Wt. of Metahnol (gms)	Amount of Glycerol Liberated (Gms)	% Conversion Of Glycerol
1	40	20	8	3.235	81.96
2	40	30	12	3.460	87.65
3	40	40	16	3.648	92.4
4	40	50	20	3.663	92.8

Parameters controlling percent yield of Heptaldehyde and Undecylenic acid

Experiments were conducted to obtain heptaldehyde and undecylenic acid by pyrolytic decomposition of castor oil at high temperatures and reduced pressure. The effect was calculated as

% Yield = (Amount Obtained/ Amount Expected) x 100

The following parameters were studied

Effect of Raw Material

The methyl esters gave better yields compared to castor oil. The lesser yields for castor oil were due to the formation of several other compounds like acrolein etc.

Effect of Reaction Duration

It was observed that there was an increase in the yields of both Heptaldehyde and Undecylenic acids as the time of reaction increased. [Table 8]

Table 8 Effect of Raw materials and Reaction Durationon percentage yield of Heptaldehyde and Undecylenic acid

Raw Material	Amount of Raw Material (gms)	Reaction Duration (hrs.)	Amount of Heptaldehyde (gms)	% yield of Heptaldehyde	Amount of Undecylenic Acid (gms)	% Yield Undecylenic acid
Castor Oil	100	1	12	34.073	14.32	25.913
	100	2	15	42.592	19	33.426
Methyl Esters	100	1	18	51.110	22.4	39.407
	100	2	20.48	58.152	24.8	43.630

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CONCLUSION

In the methanolysis the alkali catalysed method using freshly prepared sodium hydroxide as catalyst was found to economical and efficient sine it utilized only 40 % (By wt) of methanol at optimum temperature of 60 ^{0} C at 2 hrs. As compared to the use of castor oil as raw material the methyl ester gave better yields of both Heptaldehyde and Undecylenic acid.

REFERENCES

[1] Acharya KT. J Oil Tech Ass India 1977; 82.
[2] Jamieson GR and Reid EH. J Chromatograpy 1965.
[3] Das G, Trivedi RK and Vasistha AK. J Amer Oil Chem Soc 1989; 66: 938.
[4] San Irving N and Lewis R. J Sr Condensed Chemical dictionary. CBS Publishers and Distributors, New Delhi. 11th Edi; 593.
[5] Gupta and Agrawal. J Sci Ind Res 1954; 13b: 277.
[6] Kakade VV and Subrahmanyam VVR. J Oil Tech Ass India 1983; 15(4): 84.
[7] Cocks LV and Van Rede C. Laboratory hand Book for Oil and Fat Analysis, p-96. John Wiley and Sons, New York 1966.