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EFFECTS OF EXPERIMENTAL VARIABLES ON THE DEGREE OF EPOXIDATION OF ORANGE SEED OIL AND LINSEED OIL USING CLAY-SUPPORTED HYDROGEN PEROXIDE

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ABSTRACT

The effects of temperature, time, nature of solvent and nature of clay-supported hydrogen peroxide on the degree of epoxidation of orange seed oil (OSO) and linseed oil (LO) were investigated by iodine value measurements. Results show that epoxidation increases with increasing epoxidation time up to a maximum before decreasing. Epoxidation was found to be more effective at elevated temperature of 50^{0}C than at room temperature. Also, polar solvent (1,4-dioxane) was found to be a better epoxidation solvent than non-polar toluene solvent. Treated clay-supported hydrogen peroxide yielded lower iodine values showing better epoxidation than untreated clay-supported hydrogen peroxide. Optimum epoxidation conditions were epoxidation time of 4 hours using clay-supported hydrogen peroxide in 1,4-dioxane solvent at 50^{0}C where the least iodine values of 67.26 (B_1), 66.62 (B_2), 62.50 (B_3), 55.20(B_4), 51.08 (B_5) and 112.31 (B_1), 92.95 (B_2), 83.12 (B_3), 78.36 (B_4), 75.51 (B_5) for orange seed oil and linseed oil were obtained respectively.

KEYWORDS: Epoxidation, clay-supported hydrogen peroxide, orange seed oil, linseed oil.

INTRODUCTION

Vegetable oils are predominantly made up of a mixture of triesters of glycerols and fatty acids. Other minor compounds of vegetable oils are phosphatides, sterols and tocopherols. Vegetable oils are classified as drying, semi-drying and non-drying based on their iodine values. The iodine value is a numerical measure of the degree of unsaturation in an organic compound. For oils, when the iodine values are greater than 140, between 125 and 140 and less than 125, they are described as drying, semi-drying and non-drying respectively. The orange seed oil (OSO) is obtained by extraction from orange seed while linseed oil (LO) is extracted from the seeds of the flux plant. The main fatty acid present in linseed oil is linolenic acid shown as Figure 1.

$CH_3CH_2CH{=}CH\ CH_2\ CH{=}\ CH\ CH_2\ CH = CH(CH_2)_7COOH$

Figure 1. Linolenic acid.

Prisleschajew (1978) reported the direct, single step epoxidation of unsaturated organic compounds using peracetic acid or other peracids. However, the first successful use of preformed acid in epoxidation was carried out by Findley et al (1945). Teixeira et al (2002) reported the use of molybdenum-based catalysts heterogenized in silica matrixes for epoxidation. The epoxidation of cyclohexene on heterogenized molybdenum compounds have been reported by Barradas et al (1998). Investigation of catalyst recycling in the epoxidation of alkenes through precipitation with poly (ethylene oxide) has been carried out by Dallman et al (2002). Buffon and Schuchardt (2003) have reported the heterogenization of catalysts used for epoxidation of alkenes.. Studies on fermentation based processes for the conversion of fats, oils and their derivatives into biopolymers and biosurfactants have been reported in recent time (Solaiman et al, 2003).

The epoxidation of alkenes and other organic compounds containing unsaturated carbon-carbon linkage with molecular oxygen, hydrogen peroxide, alkyl hydroperoxides, sodium hydrochlorite and iodosyl benzene have been investgated in recent time and reviewed (Jorgensen, 1989; Sheldon and Kochi, 1981; Jorgensen et al, 1989). Here we present the epoxidation of orange seed oil and linseed oil with hydrogen peroxide supported on bentonite clay as oxygen donor at varying experimental conditions.

MATERIALS AND METHODS

Materials

Bentonite clay sample (moisture content, 0.86%, surface area, 15 cm^2, pH, 7.26-7.65, cation exchange capacity, 98.4 mEq/100g and oil absorption value, 45cm^3/100g) was obtained from D. Magcobar Nigeria Limited, Port Harcourt. Potassium hydroxide, sulphuric acid, hydrogen peroxide(BDH Chemicals, England), carbon tetrachloride, 1,4-dioxane, toluene (May & Baker, England) and potassium iodide, petroleum spirit (Vickers Laboratories, England) used for the study were analytical grade reagents.

METHOD

Extraction of Orange Seed Oil (OSO)

The orange seeds were obtained from orange fruits, washed with water and air-dried before peeling off the thin exocarp. They were crushed into powder and 50g each were measured using Mettler analytical balance. The orange seed oil was obtained using a soxhlet extractor with petroleum spirit as solvent. A major component of OSO is oleic acid. Elemental analysis (Found: C, 76.3; H, 12.0%. Calculated for $C_{18}H_{34}O_2$: C, 76.6; H, 12.1%)

Preparation of Clay-Supported Regents

Acid treated bentonite clay as well as an untreated sample were prepared as clay-supported regents (CSRs) following earlier reported procedures (Otaigbe et al, 2004). The chemical compositions of the treated and untreated clay-support reagents are shown in Table 1.

Characterization of the Oils

Acid number and iodine value of the orange seed oil and linseed oil were determined following earlier reported procedures (D' Allelo, 1946). The Acid number and iodine value of the orange seed oil were found to be 17.39 mgKOH/g and 85.44 respectively while those of linseed oil were 15.70mgKOH/g and 186. 07 respectively.

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Epoxidation of the Oil/Determination of Epoxy Groups of the Epoxidized Oils

Procedure reported by Udipi.(1979) was used in the epoxidation of orange seed oil and linseed oil using treated and untreated Clay-supported hydrogen peroxides in both toluene and 1, 4- dioxane solvents at room temperature and at elevated temperature of 50°C respectively at various epoxidation times. The epoxy group of the epoxidized oils was determined by measuring 25cm^3 of 1,4-dioxane into 250cm^3 conical flask. 1.0g epoxidized orange seed oil was next added to the conical flask, which was homogenized by agitation. 25cm^3 Hydrochlorinated dioxane was added to the flask, stoppered and allowed to stand for 15 minutes at room temperature. 25cm^3 neutralized cresol red-ethanol solution was added to the flask and excess hydrochloric acid was back titrated with 0.1M methanolic sodium hydroxide solution until a violet colour appeared. A blank titration was performed and the percent epoxy group was calculated using the following equation.

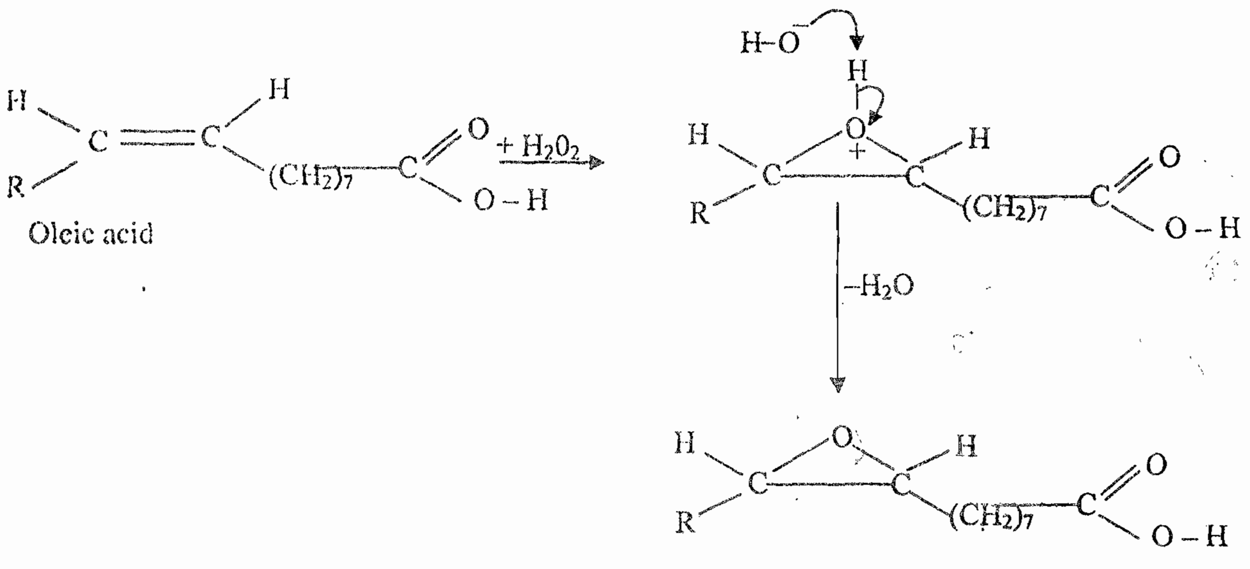
$$E = \frac{0.160(vol.of 0.1MHCl used)}{Weight of sample(g)} + 0.285(AN) \times \frac{100}{1} \ldots\ldots\ldots\ldots(1)$$

Where E = % epoxy group by weight
AN = Acid Number

The epoxy value (mgHCl/g) was calculated using Equation 2.
Epoxy value (mgHCl/g) = 22.79E .... (2)

RESULTS AND DISCUSSION

The mechanism of epoxidation of oleic acid (a component of orange seed oil is shown below:



Where R = C_8H_{17}

Results of the acid treatment of the bentonite clay used in this study have been reported (Otaigbe et al, 2004). The chemical compositions of both the treated and untreated clay-supported hydrogen peroxide are shown in Table 1.

Table 1: Chemical compositions of the clay – supported Hydrogen peroxide

Clay sample		Vol. of glacial acetic acid (cm^3)	Vol. of 30% hydrogen peroxide (cm^3)	Vol. of concentrated sulphuric acid (cm^3)
Treated	Untreated			
B_1	A_1	20	20	1
B_2	A_2	20	30	1
B_3	A_3	20	40	1
B_4	A_4	20	50	1
B_5	A_5	20	60	1

The degree of epoxidation was monitored by withdrawing 0.20g of orange seed oil and linseed oil respectively at hourly intervals to test for their iodine values. Results generally show an increase in the degree of epoxidation with an increase in epoxidation time up to a limit before the trend reverses. For instance, iodine values of orange seed oil sample B_1 using treated clay-support reagent in 1,4-dioxane solvent at room temperature (Table 1) were 76.77 at 1 hour epoxidation time, 73.66 at 3 hours, 69.16 (minimum) at 5 hours before increasing to 75.51 at 6 hours. In the case of linseed oil, under the same conditions (Table 3), iodine values were 176.07 at 1hour epoxidation time, 149.42 at 3 hours, 114.53 (minimum) at 5 hours before an increase to 118.02 at 6 hours. The increase in iodine values of both orange seed oil and linseed oil at 6 hours epoxidtion time is probably due to a reversal, ring opening and other side reactions which might occur at long epoxidation time.

The effect of nature of solvent was investigated using polar, 1,4-dioxane solvent and non-polar, toluene solvent using both treated and untreated Clay-supported hydrogen peroxides respectively at room temperature. Results indicate that 1, 4-dioxane (polar solvent) was a better epoxidizing solvent than toluene (non-polar solvent) since lower iodine values were obtained with 1,4 –dioxane when compared to toluene under the same conditions in all the cases considered. With treated Clay-supported hydrogen peroxide in toluene, orange seed oil had iodine values of 82.48, 80.26,76.77, 78.68 (Table 6, sample B_3) at 1 hour, 3 hours, 5 hours epoxidation times respectively compared to 72.65, 67.89, 62.81, 63.77 in 1,4-dioxane at 1 hour, 3 hours, 5 hours, 6 hours epoxidation times respectively (Table 2).

Table 2: Iodine Values of Orange Seed Oil During Epoxidation Using Treated Clay-Supported Hydrogen Peroxide in 1,4-dioxane Solvent at Room Temperature

Time	Iodine value of samples				
(Hours)	B_1	B_2	B_3	B_4	B_5
1	76.77	74.87	72.65	68.82	67.25
2	74.24	74.00	69.16	66.49	64.72
3	73.66	72.01	67.89	63.13	61.86
4	71.70	67.38	66.62	66.62	59.96
5	69.16	66.94	62.81	61.60	58.69
6	75.51	67.26	63.77	67.89	59.00

Similar trend was observed in the case of untreated Clay-supported hydrogen peroxide. For linseed oil at similar conditions, epoxidation in toluene gave iodine values (Table 7, B_3) of 176.39, 173.54, 171.63, 170.99 at 1 hour, 3 hours, 5 hours, 6 hours epoxidation times respectively.

The effect of the nature of Clay-supported hydrogen peroxide was investigated by determining iodine values during epoxidation using both treated and untreated Clay-supported hydrogen peroxides respectively in 1,4 –dioxane at room temperature. Results are shown in Tables 2, 3, 4, and 5 respectively.

Table 3: Iodine Values of Linseed Oil During Epoxidation Using Treated Clay-Supported Hydrogen Peroxide in 1, 4- Dioxane Solvent at Room Temperature

Time	Iodine value of samples				
(Hours)	B_1	B_2	B_3	B_4	B_5
1	176.07	159.26	148.79	143.40	135.46
2	166.56	144.35	141.18	134.20	130.39
3	149.42	125.63	120.87	118.97	111.67
4	127.85	110.08	105.33	105.01	101.84
5	114.53	93.27	91.51	92.64	90.10
6	118.02	98.35	79.95	76.46	76.77

Table 4: Iodine Values Of Orange Seed Oil During Epoxidtion Using Untreated Clay-Supported Hydrogen Peroxide in 1,4 – Dioxane Solvent at Room Temperature

Time	Iodine value of samples				
(Hours)	A_1	A_2	A_3	A_4	A_5
1	84.39	82.49	80.90	78.99	77.09
2	82.17	80.58	78.68	77.41	74.23
3	80.26	79.31	76.14	74.24	71.70
4	79.31	75.51	70.43	69.16	63.13
5	74.55	73.60	68.21	66.30	60.91
6	75.51	74.24	69.48	66.94	61.86

Tables 5: Iodine Values Of Linseed Oil During Epoxidation Using Untreated Clay-Supported Hydrogen Peroxide in 1,4-Dioxane Solvent At Room Temperature

Time	Iodine value of samples				
(Hours)	A_1	A_2	A_3	A_4	A_5
1	178.93	166.56	150.69	138.00	137.69
2	173.85	162.11	144.03	132.61	130.71
3	159.89	158.75	134.20	121.51	120.87
4	154.18	142.44	123.09	102.15	98.98
5	131.62	120.56	111.04	90.73	90.10
6	144.98	130.39	111.67	98.98	98.98

Table 6: Iodine Values Of Orange Seed Oil During Epoxidation Using Treated And Untreated Clay-Supported Hydrogen Peroxide in Toluene Solvent At Room Temperature

Time	Iodine value of samples				
(Hours)	A_4	A_5	B_1	B_3	B_4
1	86.29	85.02	83.75	82.49	81.22
2	84.71	83.44	82.17	80.90	80.58
3	83.75	81.85	80.90	80.26	78.99
4	81.85	81.22	80.26	79.31	77.14
5	80.58	80.90	84.39	76.77	76.14
6	82.36	84.39	85.97	78.68	77.41

Table 7: Iodine Values Of Linseed Oil During Epoxidation Using Treated And Untreated Clay-Supported Hydrogen Peroxide in Toluene Solvent At Room Temperature

Time	Iodine value of samples				
(Hours)	A_4	A_5	B_1	B_3	B_4
1	181.47	180.20	178.29	176.39	175.12
2	180.20	178.61	177.34	175.12	171.95
3	178.29	177.03	175.76	173.54	171.31
4	177.66	176.07	175.12	172.58	170.68
5	176.71	175.76	174.49	171.63	170.36
6	176.07	175.12	174.80	170.99	169.73

Results show that the treated Clay-supported hydrogen peroxide is more effective in epoxidation than the untreated sample since the latter yielded lower iodine values during epoxidation at different epoxidation times. In the case of orange seed oil, iodine values obtained for epoxidation using treated clay- supported reagent (Table 2, sample B_2) were 74.87 at 1 hour, 72. 01 at 3 hours, 66.94 at 5 hours and 67.26 at 6 hours compared to the higher corresponding values of 82.49, 79.31, 73.60 and 74.24 for the untreated sample. This is due to the fact that acid treatment of the clay increased the surface area compared to the untreated (raw) clay and thus provides better support characteristics. Similar results were obtained for linseed oil where the results of the treated clay- supported reagent (Table 3, B_2), iodine values were 159.26, 125.63, 93.27, 98.35 at 1 hour, 3 hours, 5 hours and 6 hours respectively, compared to the case with untreated clay supported reagent (Table 5, A_2), whose iodine values were found to be 166.56, 158.75, 120.56, 130.39 at 1 hour, 3 hours, 5 hours and 6 hours respectively.

The effect of temsperature on epoxidation of orange seed oil and linseed oil respectively was investigated by carrying out the reaction at room temperature and elevated temperature of 50°C using treated clay- supported reagent in 1, 4- dioxane solvent. Results are shown in Tables 2 and 8 for orange seed oil and Tables 3 and 9 for linseed oil.

Table 8: Iodine Values Of Orange Seed Oil During Epoxidation Using Treated Clay-Supported Hydrogen Peroxide in 1,4-Dioxane Solvent At 50°c

Time	Iodine value of samples				
(Hours)	B_1	B_2	B_3	B_4	B_5
1	74.87	73.92	68.21	66.62	61.86
2	73.53	70.43	67.26	64.40	61.23
3	68.21	67.89	66.30	62.18	59.01
4	67.26	66.62	62.50	55.20	51.08
5	69.16	68.53	66.31	56.79	55.52
6	74.24	72.65	67.89	64.08	61.23

Table 9: Iodine Values Of Linseed Oil During Epoxidation Using Treated Clay-Support Hydrogen Peroxide In 1,4-Dioxane Solvent at 50°c

Time (Hours)	Iodine value of samples				
	B_1	B_2	B_3	B_4	B_5
1	164.65	144.35	140.86	133.88	128.17
2	145.30	129.12	121.51	118.65	111.35
3	126.26	109.13	104.69	97.08	90.10
4	112.31	92.95	83.12	78.36	75.51
5	117.38	98.03	88.19	79.95	78.36
6	118.65	105.33	92.64	79.31	79.95

Results indicate that epoxidation proceeds at a faster rate and that a higher degree of epoxidation was attained at 50°C than at room temperature. This is because increase in temperature generally increases reaction rates. However, extremely high temperatures lead to the destruction of the oxirane ring due to its strained nature (Kirk, 1978). For orange seed oil, at 50°C, iodine values (Table 8, B_1) were 74.87, 67.26, 69. 16, 74.24 at 1 hour, 4 hours, 5 hours and 6 hours respectively, compared to room temperature values (Table 2, B_1) of 76.77, 71.70, 69.16, 75.51, at 1 hour , 4 hours, 5 hours and 6 hours respectively. For linseed oil, at 50°C, iodine values (Table 9, B_1) were 164.65, 112.31, 117.38, 118.65 at 1 hour, 4 hours, 5 hours and 6 hours respectively compared to corresponding values (Table 3, B_1) of 176.07, 127.85, 114.53, 118.02 at room temperature. This further shows that the epoxidation attained its optimum in a shorter time of 4 hours at 50°C compared to the time of 5 hours for epoxidation at room temperature.

The epoxidized oils were characterized for their acid number, % epoxy group and epoxy value. The results are shown in Tables 10 and 11 for orange seed oil and linseed oil respectively .Results show that the acid number decreases with decreasing iodine value while the reverse is true for % epoxy group and epoxy value in line with an earlier report (Findley et al, 1945).

Table 10: Acid Number, % Epoxy Group and Epoxy Value of the Epoxidized Orange Seed Oil Samples

Sample	Acid Number (mg KOH/g)	%Epoxy Group	Epoxy value (mg HCl/g)
B_1	14.03	1.57	35.78
B_2	13.46	1.96	44.62
B_3	7.85	2.17	44.90
B_4	5.10	2.43	52.87
B_5	3.93	2.53	55.38

Table 11: Acid Number, % Epoxy Group And Epoxy Values Of the Epoxidized Linseed oil Samples

Sample	Acid Number (mg KOH/g)	%Epoxy Group	Epoxy Value (mg HCl/g)
B_1	12.90	4.98	113.49
B_2	9.54	5.12	116.25
B_3	7.29	5.32	121.24
B_4	5.61	5.82	137.64
B_5	5.05	5.98	136.28

CONCLUSION

This study has shown that the epoxidation of orange seed oil and linseed oil is better carried out using treated clay-supported reagent than the untreated clay sample. Also, elevated temperature of 50°C and polar solvent (1,4 –dioxane) were more effective epoxidizing conditions than at room temperature and using a non- polar (toluene) solvent. Finally, epoxidation time of 4 hours, elevated epoxidation temperature of 50°C, use of polar, (1,4- dioxane) and use of treated clay-supported reagents were found to be the optimum conditions for the epoxidation of orange seed oil and linseed oil respectively.

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