

A SEPARATION OF THE SATURATED AND UNSATURATED COMPONENTS
OF COTTONSEED OIL WITH LIQUID SULFUR DIOXIDE

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INTRODUCTION

The use of liquid sulfur dioxide as an organic solvent presents a comparatively new field of investigation. L. Edelnau¹ reported almost complete separation of aromatic and cyclic hydrocarbons from paraffins and naphthenes in petroleum distillates at low temperatures with liquid sulfur dioxide. Later, Moore, Marvel, and Egloff² compared the solubility of a large number of saturated and unsaturated hydrocarbons over a temperature range with varying concentrations of the solvent. They also noted an apparent tendency for compound formation between the sulfur dioxide and the unsaturated hydrocarbons. F. de Carli³ made a study of the solubility of many unsaturated and saturated compounds, both cyclic and aromatic. He divided these compounds into three general classes as follows: those which were insoluble, those which were miscible but did not undergo a chemical reaction, and those which entered into compound formation with the sulfur dioxide. He concluded that liquid sulfur dioxide was an excellent solvent for aromatic hydrocarbons containing multiple bonds; the appearance of a definite color in the reaction

¹Edelnau, Bull. Am. Inst. Min. Eng., 2313-32, (1913)

²Moore, Marvel, Egloff, Met. Chem. Eng., 18: 396-402, (1918)

³de Carli, Gass. chim. ital., 57: 347-55, (1927)

mixture was ascribed to compound formation. Ryden and Marvel⁴ reported the use of paraformaldehyde and a 3 per cent hydrogen peroxide solution as catalysts in addition reactions, with excellent results. These investigators asserted that no evidence of addition of sulfur dioxide was obtained with compounds containing chloride, cyano, aldehyde, or ester groups. Negative results were reported with acids or acid salts. Ryden, Marvel, and Glavis⁵ showed that ascaridole catalyzed reactions between sulfur dioxide and unsaturated compounds containing chloride and cyano groups, but no satisfactory addition could be obtained between sulfur dioxide and totally substituted acetylenic linkages. Reactions did not occur when the unsaturated compound was a tri or tetra substituted olefin, even in the presence of a catalyst. These workers suggested that a carbon-oxygen double bond conjugated with the ethylenic linkage tended to block addition of sulfur dioxide across the unsaturated bond; an example of this type compound is ethyl crotonate.

Identification of compounds formed by the addition of unsaturated compounds and liquid sulfur dioxide has been successful, and a satisfactory mechanism for this reaction has been advanced. According to Staudinger and Ritzenthaler⁶, compounds similar to high molecular weight ozonides or peroxides are formed. These addition compounds or sulfones are insoluble in ordinary organic solvents, soluble in nitric and sulfuric acids without decomposition, and undergo hydrolysis in alkali-

⁴Ryden and Marvel, J. Am. Chem. Soc., 57: 2311-24, (1935)

⁵Ryden, Marvel, and Glavis, J. Am. Chem. Soc., 59: 1014-15, (1937)

⁶Staudinger and Ritzenhalter, Ber., 68B: 455-71, (1935)

line solutions to yield several compounds. These investigators reported evidence of polymers containing 2000 or more primary molecules, as determined by viscosity measurements in sulfuric acid. Ryden and Marvel⁷ have proved the presence of a hydroxyl group at the end of the polymer chain. Decomposition of the sulfone and analysis of the products by these workers have shown that one molecule of the sulfur dioxide reacts with one molecule of the unsaturated compound. High pressure was found to aid in the reaction, and the presence of light was necessary. Ascaridole, ozone in chloroform, organic peroxides, hydroxy benzenes, and hydrogen peroxide were found to be the most successful catalysts.

Marvel, Frederick, and Cogan⁸ have determined some of the products of alkaline decomposition of the sulfones. An amorphous compound, formed by reacting cyclohexene and sulfur dioxide, was found to decompose into octahydro biphenyl, dicyclo hexenyl sulfone, dodeca hydro-phenoxthin dioxide, cyclohexene, cyclohexene sulfinic and sulfonic acids, potassium carbonate, and other compounds incapable of identification. Recent experiments by Marvel and Sharkey⁹ have shown that reactions have been catalyzed by ultra-violet light in a peroxide-free reaction mixture. Analysis of polymers resulting from this reaction proved identical with the sulfone decomposition products from the reaction catalyzed by peroxides.

The use of sulfur dioxide as an organic solvent has already

⁷Ryden and Marvel, J. Am. Chem. Soc., 57: 2311-24, (1935)

⁸Marvel, Frederick, and Cogan, J. Am. Chem. Soc., 61: 1603, (1939)

⁹Marvel and Sharkey, J. Am. Chem. Soc., 61: 1603, (1939)

found extensive commercial application. It is used in the petroleum industry to dissolve olefins occurring in the light fractions of the distillate from any saturated hydrocarbons which are present. Some of the products of alkaline decomposition of the sulfones have found use as plastics; other similar products are employed as mixers for varnishes, films, or ornamental articles. Other sulfones have been combined with celluloid to reduce the inflammability of the latter.

The purpose of this work has been an attempt to utilize liquid sulfur dioxide as a selective solvent in the separation of the saturated and unsaturated components of cottonseed oil. The literature has been reviewed, and it was found that almost all work with sulfur dioxide in the field of organic chemistry has been done in connection with compound formation with this reagent. Practically all of the literature relating to sulfur dioxide as a pure solvent exists as patents, and details are meager.

Dr. E. E. Reid¹⁰ has suggested an analogy in the chemical behavior of olefins and the esters of unsaturated fatty acids. In attacking the problem, the synthesis of some high molecular weight unsaturated esters and a study of their solubility in liquid sulfur dioxide have been undertaken, as well as an investigation of the action of sulfur dioxide on cottonseed oil. Successful separation of similar saturated compounds with this reagent, and their successful recovery, would be a valuable aid to organic chemists. Possible commercial significance might result from the separation of the saturated and unsaturated components of cottonseed oil, the unsaturated portion finding use as a drying oil.

¹⁰Private communication from Dr. E. E. Reid

REAGENTS AND APPARATUS

The liquid sulfur dioxide used in this problem was a high grade commercial product. Qualitative tests for the presence of hydrogen sulfide or sulfur trioxide were negative. Samples which were run into dry containers failed to test acid in the presence of methyl orange or litmus solution, proving the absence of any moisture. The reagent was water white, and the boiling point was -10° C.

The cottonseed oil provided for experimental work was a refined oil of high purity. The physical constants determined in the laboratory are given in Table I.

TABLE I

PHYSICAL CONSTANTS OF COTTONSEED OIL

Color	-----light yellow
Sp. G.	----- 0.8735^{25}_4
F. P.	-----below -20° C
B. P.	-----above 200° C
I ₂ No.(Hanus)	-----109.3

Determination of the action of liquid sulfur dioxide on high molecular weight esters necessitated their synthesis in the laboratory. For this purpose, the butyl esters of palmitic, stearic, and oleic acids were chosen for their similarity to glycerides appearing in the oil. The ease of preparation of these esters and their approximation of the structure of a olefin were the determining factors in their choice for experimental purposes. Similar in its properties to other short chain alcohols, the slight solubility of butyl alcohol in water and its relatively low boiling point made its use desirable. For preparation of these esters, U. S. P. grade butyl alcohol was distilled, and the fraction with boiling range of $115-116^{\circ}$ C was retained for use

in esterification.

Palmitic acid of C. P. grade was available; commercial grades of oleic and stearic acids were purified before their esters could be prepared. The stearic acid was purified by dissolving the acid in ether and recrystallizing from water. Repeated crystallizations in this manner yielded a fairly pure grade acid which was white in color. The liquid oleic acid was subjected to fractional distillation under reduced pressure. The fraction boiling at 205-206°C at 25 mm. pressure was selected for use in esterification.

The alcohol was mixed with each of the acids in the proportion of one mole of acid to four moles of the alcohol. This large excess of alcohol was desirable, partially to insure complete conversion of the acid to the ester, but primarily, by utilizing the ability of the alcohol to carry over water formed in the reaction during distillation, to lessen the tendency of the ester to suffer hydrolysis. After the reaction mixture had been heated to 150°C and refluxing had begun, dry hydrogen chloride was bubbled through the mixture for catalytic effects; five grams of hydrogen chloride was used for each mole of acid. The contents of the flask were refluxed vigorously for a period of twelve hours. It was noticed that upon heating, the mixture which had been light yellow in color assumed a reddish-brown hue.

When the period of refluxing was finished, the excess of alcohol and water was distilled from the ester. This procedure was simplified by construction of a continuous distillation apparatus, a modification of a system described by Gilman¹¹. Essentially the same in all respects,

¹¹Gilman, Organic Syntheses, Collective Volume 1, (Jno. Wiley and Sons, New York, 1932), p. 259

a different type receiver was devised to satisfy the need in this apparatus. It was necessary that the receiver should allow the withdrawal of the water and that the lighter alcohol should be returned to the distillation pot. This was accomplished through the use of a section of 20 mm. glass tubing 30 cm. in length. The tube was closed at one end by a stop-cock and was connected to the reaction flask by a side arm, placed 5 cm. below the lip of the receiver. The water formed a layer on the bottom of the receiver; distillation was continued until the theoretical amount of water had been distilled from the ester.

The crude esters were dark red in color and possessed a characteristic ester odor. They were thin, oily liquids and were soluble in ethyl alcohol and ether. Purification was carried out by fractionation under reduced pressure. A standard apparatus ¹² was constructed, a 10 cm. Vigreux column being used. Pressures as low as 2 mm. were obtained through the use of a Cenco Hyvac pump. The purified butyl oleate was a light yellow liquid; the butyl stearate and palmitate were water white in color.

The physical constants of the esters are summarized in Table II.

No apparatus applicable to all phases of the problem was perfected. Since very low temperatures were necessary, reactions were carried out in dry ice-chloroform bath which was capable of producing temperatures as low as -70°C. The bath consisted of a cylindrical container insulated with magnesia within a stone crock. In some cases,

¹²Morton, Laboratory Technique in Organic Chemistry (McGraw-Hill Book Company, Inc., New York, 1938), pp.225-6

TABLE II

PHYSICAL CONSTANTS OF SYNTHETIC ESTERS

<u>COMPOUND</u>		<u>BUTYL PALMITATE</u>	<u>BUTYL STEARATE</u>	<u>BUTYL OLEATE</u>
FORMULA		$C_{15}H_{31}COOC_4H_9$	$C_{17}H_{35}COOC_4H_9$	$C_{17}H_{33}COOC_4H_9$
B. P.	Found	196-98°C (4mm)	212-15°C (6mm)	200-03°C (2mm)
	Lit. ¹³	-----	220-25°C (10mm)	173-227°C (2mm)
M. P.	Found	5-6°C	25-6°C	-15-6°C
	Lit. ¹³	5°C	27°C	-----
Sp. G.	Found	0.855 ²⁵ / ₂₀	0.855 ²⁵ / ₂₀	0.868 ²⁵ / ₂₀
	Lit. ¹³	0.862 ²⁰ / ₂₀	0.854 ²⁰ / ₂₀	0.873 ²⁰ / ₂₀
n_D	Found	1.400 ²⁵	1.436 ²⁵	1.489 ²⁵
	Lit. ¹³	1.409 ²⁰	1.442 ²⁰	-----
M_D	Found	93.9	102.1	103.9
	Lit. ¹⁴	96.2	103.1	100.9
I ₂ No.	Found	1.58	2.03	74.3
	Lit. ¹³	-----	1.96	76.8

¹³Courtesy of Commercial Solvents Corp., New York City

¹⁴Gilman, H., Organic Chemistry, Vol 2, (John Wiley and Sons, New York, 1938), p. 1737

it was desirable to use vessels surrounded by asbestor sheet, where such low temperatures were not desired. In order to prevent pressure from the evaporation of the liquid sulfur dioxide, the use of a closed system had to be abandoned. Pyrex glassware was employed in all operations.

EXPERIMENTAL

THE ACTION OF LIQUID SULFUR DIOXIDE ON SYNTHETIC ESTERS

Efforts to determine the solubility of heavy esters in liquid sulfur dioxide were chosen as the first step in the experimental work. Small amounts of the pure esters already described were selected and reacted with varying concentrations of the solvent. It was found that the butyl oleate formed a completely miscible solution with the sulfur dioxide, but an appreciable darkening in the color of the mixture was noticed. After the flasks were allowed to remain in the cold bath from one-half to three hours, the mixture was removed and the sulfur dioxide was allowed to evaporate at room temperature. The ester was dissolved in ether, washed with water several times, recovered from the ether, and carefully examined. A solution of the ester in ether was allowed to stand with sulfur dioxide, and a completely miscible solution resulted, although ether alone is insoluble in liquid sulfur dioxide.

Larger, more accurately weighed samples were taken for quantitative experiments with the sulfur dioxide. Fifteen to sixteen gram samples were weighed, representing approximately 0.05 moles of the ester. The reaction was carried out with measured volumes of sulfur dioxide, according to the procedure already described. A summary of the results observed are shown in Table III:

TABLE III

THE ACTION OF LIQUID SULFUR DIOXIDE ON BUTYL OLEATE

<u>Run</u>	<u>Wt. of ester</u>	<u>Vol. SO₂ added</u>	<u>Wt. SO₂ Absorbed</u>	<u>I₂ no. of pure ester</u>	<u>I₂ no. of reacted ester</u>
1	14.52 g	20.2 cc	0.1 g	74.3	74.1
2	16.38 g	20.4 cc	0.1 g	74.3	74.0
3	15.83 g	23.5 cc	0.0 g	74.3	74.3
4	16.64 g	26.1 cc	0.05 g	74.3	74.1
5	14.97 g	30.8 cc	0.08 g	74.3	74.2

Examination of these data indicated that the tendency for compound formation between the ester and sulfur dioxide under the experimental conditions imposed was negligible. Since the proposed mechanism of an additive reaction requires one mole of sulfur dioxide for each mole of reacted ester, the minimum amount of sulfur dioxide which might have been absorbed by these samples in a reaction was 3.g. In no instance was the increase in weight greater than 0.1g., less than three per cent of the theoretical amount. The close check afforded by the iodine numbers furnished further evidence to discount any compound formation.

These reactions were performed in an open system in order to maintain atmospheric pressure; the sulfur dioxide was evaporated at room temperature to avoid any possibility of reaction by heating the reagents. It was found that protection of the mixture from sunlight lessened the tendency of coloration in the solution. In one group of

three runs, a closed system was employed, and the reactants were allowed to stand in a lighted room for fifteen hours. Examination at the end of this time revealed that a portion of the ester had separated as an amorphous, light colored, semi-solidified mass, which floated on the surface of the residual liquid phase. This solid substance was separated, washed with sulfur dioxide, and extracted with ether. Evaporation of the ether over a steam bath left a light yellow solid with an iodine number of 7.32. Application of heat caused decomposition into a black, resinous, water-soluble mass, in contrast to the unreacted ester which is stable at high temperatures and which is very insoluble in water. These observations indicated a compound formation between this group of ester-sulfur dioxide mixtures.

Similar experiments were carried out between liquid sulfur dioxide and butyl stearate and butyl palmitate. Upon addition of sulfur dioxide to the ester, a white solid mass separated from the solution and floated on the surface of the liquid. Separation was very easy, for the solid did not melt rapidly at room temperature. In each run the weight of the separated ester equaled the weight of the ester used in the test, and evaporation of the liquid sulfur dioxide left no residue. Pressure and heat were applied to sample mixtures, but no effect was produced by the agents.

A solution consisting of a mixture of the saturated and unsaturated esters was subjected to treatment with the sulfur dioxide. Various proportions of each ester were used in separate tests, and the degree of separation was determined by the weights of the resulting fractions and the iodine numbers of these fractions. Results from five

sample runs are shown in Table IV.

The concentrations of the esters were varied in an effort to determine any effect the mutual solubilities of esters might have upon the solution of the unsaturated ester in the liquid sulfur dioxide, since a very small quantity of the unsaturated ester in a large amount of the saturated might not be dissolved by the sulfur dioxide. It was found that this possibility did not exist, through runs made in the manner previously described. Results showed that after the esters had been reacted with sulfur dioxide, subsequent washings of the saturated portion with small amounts of pure sulfur dioxide resulted in virtually quantitative separation of the components. Larger volumes of sulfur dioxide were found to facilitate this separation.

In further experiments the use of ether as a solvent was studied. It was found that separation through this means was no more complete, but a decided advantage lay in ease of removal of the sulfur dioxide from the reaction mixture. Much more complete recovery of the esters resulted from dissolving the ether-sulfur dioxide mixture in water, after the saturated ester had been removed. The free esters cannot be washed with water, since they have a tendency to form emulsions, making their recovery difficult. The use of a volatile solvent was found to eliminate this handicap; the most successful method of removing the sulfur dioxide was found to be its solution in water, and subsequent distillation of the solvent to give the free ester. In this manner the possibility of compound formation through using heat or allowing the mixture to stand for hours before the sulfur dioxide was completely evaporated was eliminated.

TABLE IV

THE SEPARATION OF SYNTHETIC ESTERS WITH LIQUID SULFUR DIOXIDE

<u>RUN</u>	<u>WT. OF SAMPLE</u>	<u>PER CENT BUTYL OLEATE</u>	<u>PER CENT BUTYL STEARATE</u>	<u>PER CENT BUTYL PALMITATE</u>	<u>WT. ESTER DISSOLVED</u>	<u>I₂ NO. OF MIXTURE</u>	<u>I₂ NO. OF DISSOLVED ESTER</u>	<u>PER CENT SEPARATION</u>
1	15.1 g	50	50	--	7.13 g	38.65	74.03	95
2	15.5 g	50	--	50	7.30 g	36.94	74.18	94
3.	20.2 g	50	23	27	9.92 g	38.05	74.05	98
4	18.3 g	66	16	18	12.30 g	49.27	74.20	98
5	20.1 g	75	5	20	14.81 g	56.12	74.15	97

THE ACTION OF LIQUID SULFUR DIOXIDE ON COTTONSEED OIL

Hilditch and Jones¹⁵ reported the composition of cottonseed oil consisted of 60 per cent glycerides containing palmityl radicals and two unsaturated, eighteen carbon radicals, either linoyl or oyl. Fifteen per cent of the oil existed as a di-palmito olein or linolein, and the remaining 24 per cent was made up of totally unsaturated glycerides. The fact of the solubility of unsaturated esters of high molecular weight fatty acids in sulfur dioxide having been established, separation of the components of cottonseed oil was attempted.

The addition of the sulfur dioxide to the oil did not darken the solution in color, generally an indication that some solution or reaction is taking place. Samples varying from 10 to 40 g. of the oil were used, and the sulfur dioxide was added in quantities of equal volume to the oil, and this amount was increased until a ratio of one part of the oil to five parts of the sulfur dioxide was reached. The two liquids remained totally immiscible under these conditions, and prolonged standing of the reactants in the bath caused the oil to solidify on the surface of the liquid sulfur dioxide. After remaining on the bath an hour, a turbidity became apparent in the sulfur dioxide layer. The two phases were separated, and after the sulfur dioxide was evaporated, no residue was left. Evidently, the cloudiness of the sulfur dioxide layer had been caused by the partial freezing of the solvent. Determination of

¹⁵Hilditch and Jones, J. Soc. Chem. Ind., 53: 13-21 T, (1934)

the iodine numbers of the reacted oil indicated that no separation had been obtained. Table V gives data from five sample runs.

TABLE V

THE ACTION OF LIQUID SULFUR DIOXIDE ON COTTONSEED OIL

<u>Run</u>	<u>Weight of oil</u>	<u>Vol. SO₂ added</u>	<u>Wt. SO₂ absorbed</u>	<u>I₂ No. of pure oil</u>	<u>I₂ No. of reacted oil</u>
1	15.3 g	34.7 cc	0.1 g	109.3	109.1
2	20.4 g	50.4 cc	.0 g	109.3	109.3
3	25.8 g	75.8 cc	.11 g	109.3	109.0
4	32.2 g	80.3 cc	.12 g	109.3	109.1
5	40.9 g	96.7 cc	.1 g	109.3	109.2

Solutions of cottonseed oil in acetone, ethyl ether, ethyl alcohol, and ethyl acetate were treated with sulfur dioxide without positive results. A closed system was employed in further experiments; pressures calculated as high as seven atmospheres were imposed upon the reaction mixture, but none of the oil was dissolved by the sulfur dioxide.

THE ACTION OF SULFUR DIOXIDE ON THE ACIDS OF COTTONSEED OIL

Samples of 100 to 200 g. of the oil were saponified, and the free acids were obtained. The most efficient procedure consisted of heating the oil up to 125°C and adding caustic soda to completely saponify the oil. A slight excess of the alkali was used for best results. The resulting soap was dissolved in hot water and filtered. The filtrate was heated, and concentrated hydrochloric acid was added until the

solution was definitely acidic. Upon acidification the free fatty acids rose to the top of the mixture and were extracted with ether. This ether solution was washed until it was neutral; it was then dried in a vacuum desiccator until all turbidity had disappeared. Evaporation of the ether over a steam bath left the free acids of the oil. An average yield of 85 per cent theoretical was obtained in this method of saponification.

The mixture consisted of 98 per cent palmitic, stearic, and oleic acids, and it was a light yellow, oily solid at room temperature. In the liquid state the color changed to a light red. The acid mixture had an iodine value of 110.9, slightly higher than the cottonseed oil.

The acids were tested for solubility in liquid sulfur dioxide by the general procedure used throughout the problem. All attempts to dissolve the unsaturated acids proved futile, despite the use of volumes of sulfur dioxide ten times as great as the volume of the acids present. Any possible effect of pressure, temperature, or light was investigated, but no positive results were obtained. The acids solidified in the liquid sulfur dioxide and were recovered quantitatively. Volatile solvents were ineffectual as agents to aid in the solution of the linoleic and oleic acids in the sulfur dioxide.

THE ACTION OF LIQUID SULFUR DIOXIDE ON THE ESTERS

PREPARED FROM THE ACIDS OF COTTONSEED OIL

Esterification of the acids of cottonseed oil and the separation of these esters with liquid sulfur dioxide were selected as the next object of experimental work. The butyl esters were prepared in the manner already described for esterification. Yields of 78 per cent of the theoretical amounts were obtained in the reactions.

The esterified mixture had an iodine number of 106.3, slightly lower than the value for the free acids. The esters were light red in color, and they remained in a liquid state at temperatures as low as 0°C.

Qualitative tests with the liquid sulfur dioxide and esters indicated the separation of a solid phase from the solution, similar to that separation obtained from the mixtures of synthetic esters. The saturated layer separated from the liquid within fifteen minutes after the sulfur dioxide was run into the reaction flask. A very serious problem arose when attempts were made to separate the solid from the liquid portion. The problem resolved itself into one of the forcing the solid out of solution rather than the expected difficulty of bringing about the solution of the unsaturated components in the solvent. At room temperature and for the first few minutes after the sulfur dioxide-ester mixture was placed in the bath, the reactants existed in the flask as completely miscible substances. Observations disclosed a tendency for the separating portion of the ester to remain dispersed throughout the solution rather than as an aggregation of the solid on the surface of the mixture. A further obstacle was discovered with the fact that the solid phase possessed a very low melting point, making experimental work at room temperature impossible.

Ordinary means of filtration proved useless, for the funnel could not be kept at temperatures low enough to prevent the melting of the solid phase. The extremely cold solution froze the finest texture filter paper. This fact made the use of an aspirator worthless. A leaf filter tightly packed with glass wool was constructed, but the rapid evaporation of the liquid sulfur dioxide when the pressure was

reduced caused solidification of the entire mixture, which was not desirable. A search was begun for a selective solvent which would facilitate the separation of the two components. The ideal solvent would dissolve the solidified saturated ester without lessening the solubility of the unsaturated ester in the sulfur dioxide. Other desirable features sought for in the solvent were volatility and solubility in water.

Chloroform, benzene, dioxane, acetone, ethyl acetate, ethyl alcohol, and diethyl ether were tested under identical experimental conditions. Acetone, ether, and ethyl acetate proved most satisfactory, and these three were chosen for use in further experiments. None of the reagents possessed all of the desirable qualities, but their effect on the ester-sulfur dioxide mixture presented very definite possibilities of aid in the attempted separation.

Ten to twelve gram samples of the esters were dissolved in the solvents, and sulfur dioxide added to the mixture in an effort to determine the quantity of the solvent which was most efficient. It was found that the amount of solvent most efficient was in the ratio of one volume of the ester to three volumes of the solvent. An amount of sulfur dioxide equal to the combined volumes of the solvent and ester was observed as the minimum amount of sulfur dioxide efficient in bringing about separation; faster and more complete reaction took place in a large excess of the sulfur dioxide.

Subsequent determinations resulted in the choice of acetone as the most desirable solvent. Acetone favored the formation of a more definite solid phase in the presence of the sulfur dioxide; its volatility and

solubility in water made recovery of the dissolved ester much easier and more satisfactory.

The separation of the finely divided solid in the solution was accomplished by means of an improvised filtration apparatus. The apparatus to be used consisted of a filter stick 8 cm. in length, containing no packing or constrictions. The lower end of the stick was covered by a piece of tightly bound coarse cloth, and a piece of finely woven cloth was fastened over the upper end of the filter. The stick was immersed in the reaction flask, and the filter was connected to a dry flask. This receiver was separated from the aspirator by a trap to prevent any water from being sucked back into the reaction flask. One of the chief advantages of the apparatus was that it enabled extractions to be made with the reaction vessel remaining in the ice bath.

When the aspirator was opened, the liquid portion was slowly drawn up through the filter. Most of the solid matter was caught by the first piece of cloth; any fine particles which escaped through into the tube were removed by the second cloth. When all of the liquid had been withdrawn from the flask, 30 cc. of pure sulfur dioxide was added, and the extraction was repeated. Addition of at least two volumes of sulfur dioxide was necessary for complete solution of the unsaturated esters.

The separated solid was an amorphous, yellow-white material which melted below room temperature. It was dissolved in ether, washed with cold water several times, and dried in a vacuum desiccator. The ether was evaporated over a steam bath. This procedure left the ester as a light red liquid.

The residual liquid, containing the unsaturated esters, was added

to water to remove the sulfur dioxide and any excess solvent. When the wash water tested neutral to indicators, the ester layer was separated and extracted with ether, washed again, and dried. Evaporation of the ether yielded a reddish-brown liquid.

A summary of five sample runs is given in Table VI.

Inspection of data in the table shows that an almost quantitative separation has been obtained of the saturated and unsaturated esters of cottonseed oil through the use of liquid sulfur dioxide. The iodine numbers of the saturated fractions indicate that almost all of the unsaturated esters have been removed. The values determined for the unsaturated esters did not increase as much as had been expected. Several possible explanations may be offered for this discrepancy. Tendency for compound formation was much more pronounced in experiments with these esters than in any case previously encountered. This tendency must be due to the presence of the linoleic radical with its two double bonds. Especial care was exercised in these experiments, the effects of light, heat, and pressure being eliminated as much as possible. Incomplete removal of the water or acetone from the ester would lower the value of the iodine number considerably.

In several instances where runs were made in the presence of bright sunlight and the sulfur dioxide was not removed immediately from the mixture, compound formation resulted in the solution. Extraction of the solid formed in this manner yielded a light colored, amorphous solid with a melting point above room temperature. Decomposition resulted when the material was heated, and it was soluble in water. Analysis of these compounds was not attempted in this problem.

TABLE VI

THE SEPARATION OF COTTONSEED OIL ESTERS WITH LIQUID SULFUR DIOXIDE

<u>RUN</u>	<u>WT. OF SAMPLE</u>	<u>WT. OF SATURATED ESTER</u>	<u>WT. OF DISSOLVED ESTERS</u>	<u>I₂ NO. OF PURE ESTER</u>	<u>I₂ NO. OF SATURATED ESTERS</u>	<u>I₂ NO. OF DISSOLVED ESTERS</u>	<u>CALCULATED I₂ NO. FOR ESTERS</u>	<u>VOL. RATIO SO₂-ESTER ACETONE</u>
1	13.4 g	3.26 g	9.22 g	106.3	11.0	116.4	126.4	6-1-2
2	12.6 g	3.24 g	9.02 g	106.3	8.6	118.2	126.4	8-1-3
3	15.7 g	4.22 g	11.22 g	106.3	7.7	119.8	126.4	8-1-4

SUMMARY

The butyl esters of palmitic, stearic, and oleic acids were prepared, and the solubilities of these esters in liquid sulfur dioxide were determined. It was found that quantitative separation of the unsaturated ester from the saturated esters was possible through the use of liquid sulfur dioxide.

Cottonseed oil was found to be insoluble in liquid sulfur dioxide under similar experimental conditions, despite the presence of 24 per cent of the composition of cottonseed oil as totally unsaturated glycerides. Application of heat and pressure had no effect upon the mixture of cottonseed oil and sulfur dioxide.

The acids obtained by the saponification of cottonseed oil were found to be insoluble in liquid sulfur dioxide under the conditions imposed in the laboratory. These results check with the reports in literature; no data is available concerning a successful solution of an organic acid in sulfur dioxide.

The butyl esters prepared from the free acids of cottonseed oil were separated through the use of sulfur dioxide. An efficient method for the separation of the saturated and unsaturated esters has been devised, and quantitative results are possible through use of this apparatus. The action of acetone as a solvent in the separation has been found to facilitate the separation.

Evidences of compound formation between the unsaturated esters and sulfur dioxide have been observed, and definite substances with different physical properties have been isolated. Pressure, heat, and the presence of sunlight were found to favor compound formation. Analytical tests were not run on these compounds in the problem.

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