A Spectrophotometric Study on the Thermal Dehydrobromination of Allylic-Brominated Soybean Oil

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Quite recently, Nanavati, Nath, and Aggarwal[1] have shown that the allylic bromination of a series of methyl esters of fatty acids with N-bromosuccinimide (NBS), followed by the thermal dehydrobromination, gave the corresponding conjugated esters. From the results of ozonolysis of the debrominated products, they have assumed that the bromination occurred in the allylic position farthest from the carboxylic group when an equivalent amount of NBS was used. Furthermore they have extended this series of reactions to various oils (mustard seed, peanut, olive, neem, karanja, tobacco seed, safflower oils), and shown that the bromo oils could be effectively debrominated by heating in pyridine, quinoline, or 2:4:6-collidine. The products from safflower and tobacco seed oils partially gelled during the process and the films of all the treated oils dried in wrinkled patterns.

Previously the present authors[2] reported that soybean oil brominated with the same brominating agent produced a conjugated oil by heating alone and that its drying properties and characteristics were greatly affected by conditions under which the debromination was carried out. In addition, some spectrophotometric observations were also reported. The present spectrophotometric study was undertaken to provide more detailed information regarding the behavior ot conjugated fatty acids produced during the thermal dehydrobromination af various temperatures.

Experimental

Materials. For this investigation, three samples of brominated soybean oil with different bromine contents were prepared according to the procedure described in the last paper[2] of this series. One of the samples contained bromine in a ratio of its one atom approximately to one double bond, and the others in a ratio of it approximately to two double bonds. The details were as follows:

Sample-A: Br, 28.3%; diene, 6.9%; triene, 0.9%; tetraene, 0.3%; total, 8.1%

Sample-B: Br, 16.7%; diene, 5.1%; triene, 0.3%; tetraene, 0.3%; total, 5.7%

Sample-C; Br, 17.4%; diene, 5.8%: triene, 0.4%; tetraene, 0.3%; total, 6.5%

Procedure. The thermal debromination of these brominated oils was carried out at temperatures of 120°C., 150°C., 200°C., and 250°C. for varying intervals of time in the following manner. About 75 g. of the brominated oil, at room temperature, was placed in a distilling flask, and the flask was evacuated to a pressure of about 10 mm. by a vaccum pump. With the pump working, the flask was immersed in a metal-bath kept at the given temeratures. At frequent intervals, samples were withdrawn and examined spectrophotometrically for conjugation and analytically for bromine content[8]. The optical density of the products was determined on a Shimazu photo-electrical spectrophotometer (QB-50), using cyclohexane as a solvent. And then the amounts of conjugated fatty acids were calculated, assuming that the spectra of naturally conjugated fatty acids and artificially conjugated, bromine-containing acids are essentially the same, and all their values are expressed on a bromine-free basis.

Results and Discussion

The respective changes that occur in bromine content and total conjugation content as the debromination progresses are shown in Fig. 1 and 2.

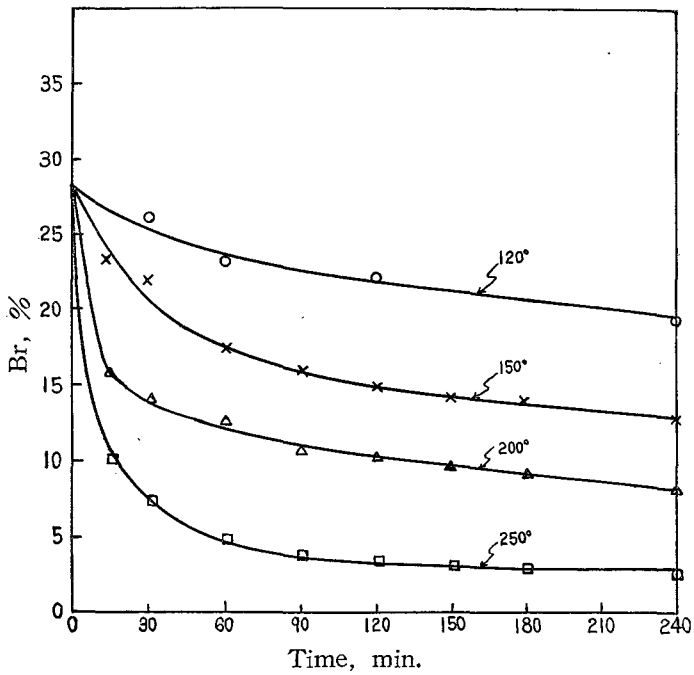

Fig.1. Effect of time and temperature on the residual bromine content.

Examination of Fig. 1 shows that the debromination rcaction at a higher temperature of 200°C. or 250°C. proceeds rapidly, and that in 15 minutes it reaches a steady state suggesting that actual debromination is almost concluded, while at a lower temperature of 120°C. or 150°C. it proceeds less rapidly and does not reach a steady state in 2 hours later. As might be expected, the amount of removed bromine tends to increase with elevating temperature, as shown in Table I.

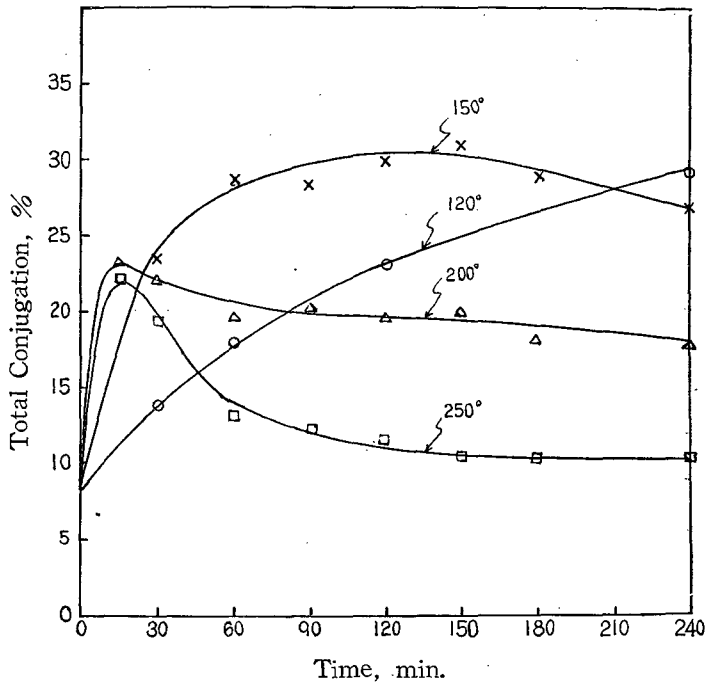

Fig.2. Effect of time and temperature on the total conjugation content.

Table I

Effect of Temperature on the Removal of Bromine

Sample	Temperature °C.	Br removed, %				
		1 hr.	2 hrs.	3 hrs.	4 hrs.	6 hrs.
A	120	19	20	—	30	32
B	120	35	45	—	51	54
A	150	38	46	50	55	—
C	150	53	58	69	76	—
A	200	54	64	67	71	—
B	200	79	87	89	—	—
A	250	82	86	89	93	—
B	250	79	82	82	83	—

However, the debromination is by no means completed, even on prolonged heating at relatively high temperatures. The difficulty which arises in the later stages of the debromination may be probably due to the formation and/or the concentration of such bromides as are debrominated less readily than those of allyl brominde type which would be expected to be preferentially formed during the bromination with NBS. Such less reactive bromides may result from the addition of bromine during the bromination or from the addition of

hydrogen bromide formed during the subsequent debromination. Furthermore, it is possible that the destruction of the structure of allyl bromide type takes place through a modified Diels-Alder's reaction of brominated, conjugated fatty acids with conjugated acids newly formed during that processing. In order to explore one of these possibilities, the thermally debrominated oil was treated with zinc in the presence of an equal volume mixture of methanol and ether with the possibility of eliminating the bromine atoms situated on adjacent positions in the carbon chain. The experimental conditions and results are summarized in Table II.

Table II

Properties of Thermally Debrominated Soybean Oil, before and after Treatment with Zinc

No.	Treatment	Br, %	Br removed, %	Conjugation, %			
				Di-ene	Tri-ene	Tetra-ene	Total
1.	Sample-A debrominated, at 150°C., 4 hrs.	17.2		19.7	2.5	1.8	24.0
2.	No. 1 treated with Zn. at about 35°C., 3 hrs.	11.4	34	19.8	5.1	1.9	26.8
3.	Sample-A debrominated, at 150°C., 4 hrs. (refined).	18.4		20.0	4.0	3.1	27.1
4.	No. 3 treated with Zn, at about 35°C., 6 hrs.	8.4	55	21.0	5.1	2.9	29.0

It may be assumed that the thermally debrominated oil contains a considerable amount of compounds of vic-dibromide type, which are generally less reative than those of allyl type, because the residual bromine can be considerably removed by treating with zinc as shown in Table II.

It appears from Fig. 2 that at lower heating temperatures the total conjugation content gradually increases with an increase in the amount of removed bromine, while at higher temperatures it reaches rapidly a maximum and then rather decreases, and that its maximum point coincides with the beginning of the steady state of the debromination. In Table III, there are recorded for each sample both the maximum conjugation produced during heating at the above-mentioned temperatures and the time taken for it to be reached.

Table III

Effect of Temperature on Maximum Conjugation and Time Required

Sample	Temperature °C.	Maximum conjugation, %	Time required, m.
A	120	33	360
B	120	21	360
A	150	32	150
C	150	25	240
A	200	23	15
B	200	22	30
A	250	22	15
B	250	23	15

It is apparent from the data in Table III that a maximum conjugation of about 33% is produced for sample-A by heating at 120°C. for 6 hours or at 150°C. for 2.5 hours; whereas by heating at higher temperatures (200°C. and 250°C.) much less amount of conjugation (22-23%) is produced for both sample-A and -B. It would be noted that heating at higher temperatures is suitable for eliminating bromine but not for producing conjugation.

For illustrating each behavior of three types of conjugation during the debromination, conjugated diene, triene, and tetraene contents plotted against the time are shown for sample-A in Fig. 3, 4, and 5 respectively.

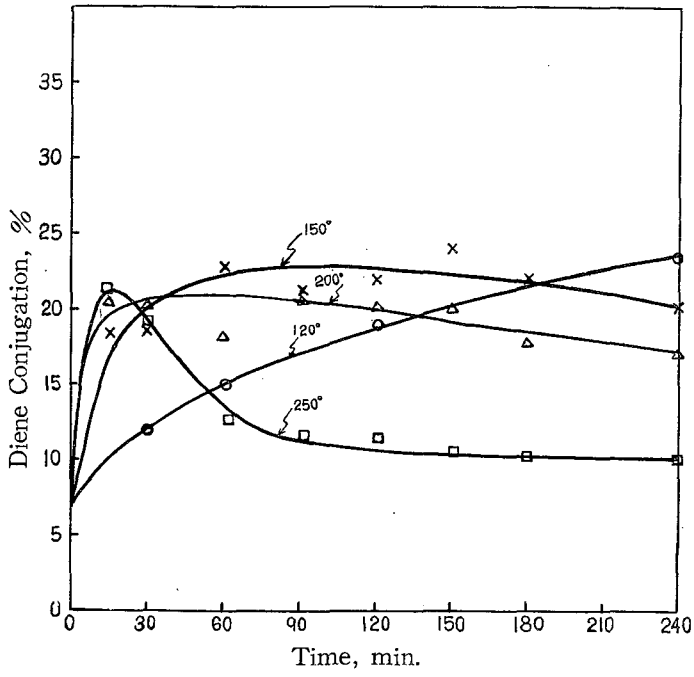

Fig. 3. Effect of time and temperature on the diene content.

It is obvious from these Figures that the thermal stability of conjugated acids depends not only on temperature, but also on the degree of conjugation. Within the range of the temperatures empolyed, diene content reaches sooner or later a maximum value (20%) depending upon the heating temperature, and at 250°C. the content reaches suddenly this value and then decreases. Triene content, at lower tem-

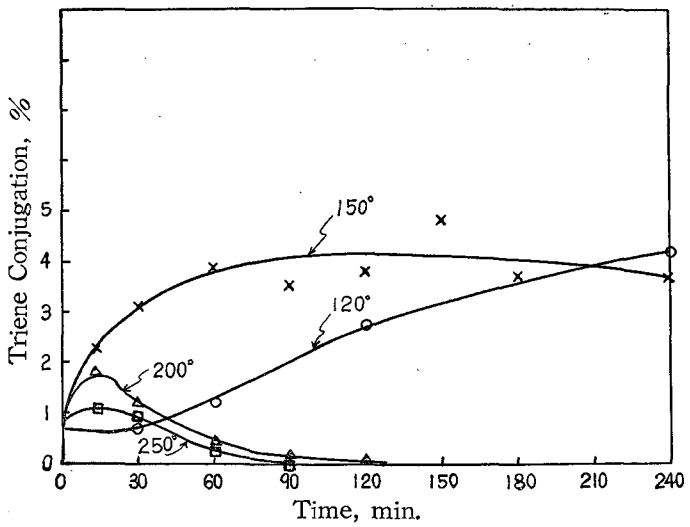

Fig. 4. Effect of time and tempenature on the triene con tent.

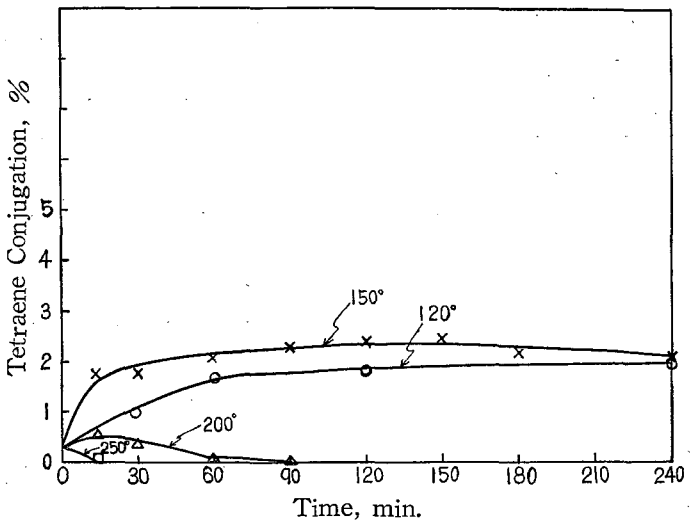

Fig. 5. Effect of time and temperature on the tetraene content.

peratures, reaches a maximum value (about 5%) which is much lower than one would expect on the basis of the content of linoleic acid in the original oil. At higher temperatures, it at first increases onyl slightly and then decreases. Tetraene conjugation, at lower temperatures, behaves in a manner similar to diene, but at 250°C., its content decreases at once. These decreases in conjugation which occur in the course of the debromination suggest that the conjugation undergoes destruction more rapidly than it is formed during the reaction. This trend becomes more remarkable with an increase in both temperature and the degree of conjugation.

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アリリック一臭素化大豆油の加熱脱臭素反応の分光光度計による研究

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前報において，*N*- ブロムコハク酸イミド（*NBS*）によって臭素化した大豆油の加熱脱臭素反応につき述べ，脱臭素油の特性や乾燥性に影響する諸因子につきやや詳細に論じた。

本報は，主に加熱脱臭素反応中の共役酸の挙動を分光光度計により検討したものである。すなわち，*NBS* によって臭素化した大豆油（臭素含量，16.7%，17.4%，および28.3%）を120°，150°，200°，および 250° の各温度において加熱脱臭素を行い，時間による共役酸生成量の変化を分光光度計により測定した。その結果，温度の上昇とともに脱臭素率は増加するが，共役酸生成は，これに伴わずにかえって減少することを認めた。120° の比較的低温，6時間で全共役酸33%を含む油が得られた。250° の比較的高温では，15分の短時間で全共役酸21%の油が得られたが，加熱時間の延長とともにかえってその含有量は減少した。勿論この減少は生成共役酸の重合に基くものと思われる。臭素含量は，前者の場合には28%より15%に，後者の場合には15分間で10%まで減少した。

なお個々の共役酸の熱に対する安定度は，温度および共役の程度に支配される。ジエンは高温においても比較的安定であるが，トリエンおよびテトラエンは温度によって著しく影響され，特に高温においては重合し易く，時間とともにその含有量は減少し，ついには全く消失した。

加熱脱臭素油を亜鉛と処理すると，さらに脱臭素が起ることから，加熱脱臭素油は，正常の臭化アリル型より脱臭素され難い *vic*- 二臭化物型のものを若干含有するものと推定した。反応後期において起る脱臭素の困難性は，この存在に基くものと考えられる。