TABLE V

Polyurethane Foams from Hydroxyethylated Dimer Acids

Foam nos.	Premix			Catalyst	Water	Physical properties				
	Hydroxyethylated dimer acids		Mole ratio, OH/NCO	Triethylene, diamine, wt. % of polyester	Wt. % of polyester	Area shrinkage, %	Density lb./ft³	Compression modulus, psi	Load required for 25% compression, psi	Compression set test test % of original height
	Sample no.	Wt %								
6	2[a]	64	0.32	0.6	2.9	3	2.7	1.2	0.6	50
7	3[a]	82	0.32	0.6	3.1	....	2.2	1.0	0.4	50
8	4[a]	67	0.32	0.5	2.5	8	2.3	0.7	0.15	50
9	5	63	0.33	0.3	1.5	16	4.4	13.4	3.5	50
10–12	1	69	0.20	1.4	2.9	0	2.1–2.2	3.1	1.2	44–45
13	1	69	0.20	1.7	3.9	0	2.2	3.1	1.1	.....
14–16	1	74	0.25	1.3	2.6	0	2.3–2.5	2.0–2.3	0.9	46–50
17–18	1	74	0.25	1.6	2.8	0	2.0	.....	.....	.....

[a] One-shot procedure was used.

In the hydroxyethylation of dimer acid, short reaction time and low temperature led to low viscosity and high hydroxyl number. Longer reaction time and high temperature gave high viscosity and low hydroxyl number (Table I).

Foam Nos. 6 to 8 (Table V) (7) showed an average density of 2.4 lb/ft³ and did not recover after 22 hr compression at 70C (compression set test = 50). Accordingly, the mixing order was reversed (Table IV) to give polymerization an opportunity to begin before the evolution of CO_2. Also, some residual acidity of the starting material (Table II, No. 1) was expected to be more favorable for crosslinking. Foams prepared with reversed mixing order Nos. 10 to 18 (Table IV) gave no area shrinkage, had an average density of 2.2 lb/ft³, and showed somewhat improved compression set tests. Foams made with 2.0 ml of Nacconate were more flexible than those made with 2.5 ml.

Foam No. 9 with compression modulus 12.4 had properties like those of a tennis ball.

The preparation of polyurethane foams depends on the starting materials used and on how the ingredients are mixed together to obtain the proper ratio of polymerization to evolution of carbon dioxide. Although results obtained from small-scale experiments may not duplicate those with large-scale mixing machines, because of the large number of variables involved (8) our small-scale exploratory experiments have shown that low-density, flexible, polyurethane foams can be prepared by a very direct route from dimer acid.

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Infrared Spectra and Gas Chromatography of Some Oxygenated Fatty Acid Derivatives[1]

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Abstract

Infrared spectra of hydroxy-, acetoxy-, oxo-, and unsaturated oxo-stearic acid derivatives were studied, and their purities were checked by gas-liquid chromatography.

INFRARED spectral studies of oxygenated fatty acids and their derivatives have been carried out by a number of workers (1). These studies included the saturated fatty acid derivatives (2,3,4,5,6), unsaturated fatty acid derivatives (7,8), *trans*-acids (9,10), linoleate (11), fatty alcohols (4), oxostearic acid derivatives (12), unsaturated oxostearic acids (13), hydroxy fatty acids (8,14,15), ricinoleate (16), ricinelaidate (17), branched chain fatty acids (18), epoxy fatty acids (14,19), glycerides (9,20), hydroperoxides (21), oxidation products of methyl oleates (22), methyl linoleate (23,24), and fats (25). In this report, the infrared spectra of some of the oxygenated fatty acids will be given. Their purity was checked by gas-liquid chromatographic analysis.

The infrared spectra of the oxygenated fatty acids were obtained at 24 ± 1C with a Beckman Model IR-7 spectrophotometer equipped with sodium chloride optics. They were studied as Nujol pastes unless otherwise indicated. Although perfect cancellation of Nujol absorption may occur with this instrument, results at ν C—H (about 3000 cm^{-1}) and δ C—H (about 1350–1500 cm^{-1}) were not conclusive. Therefore, these regions will not be discussed in detail (Table I).

Materials and Methods

Methyl 2-acetoxystearate. This compound was synthesized from stearic acid by the method of Mendel and Coops (26). The stearic acid was purified through methylation and repeated distillation under vacuum; mp 69.6C. The methyl 2-acetoxystearate of 90% purity was subjected to gas-liquid chromatography on a 10-ft silicone rubber column at 235C. It was purified by gas chromatography on a 5-ft preparatory silicone rubber column at 228C and 18 psi helium flow, 200 mA, sensitivity ×8. A 50 λ melted sample was in-

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TABLE I[a]

Gas-Chromatographic Data[b]

Ester	°C	Retention time (min)
Stearate	239	4.5
2-Acetoxy-stearate	239	7.9
12-Hydroxy-stearate	239	7.4
12-Acetoxy-stearate	239	8.7
12-Hydroxy-*cis*-9-octadecenoate	239	7.2
12-Hydroxy-*trans*-9-octadecenoate	239	7.1
12-Acetoxy-*cis*-9-octadecenoate	239	8.2
Stearate	240	4.3
9-Oxo-stearate	242	6.7
10-Oxo-stearate	240	6.7
12-Oxo-stearate	240	7.0
12-Oxo-*cis*-9-octadecenoate	240	7.4[c]
12-Oxo-*trans*-9-octadecenoate	240	7.8

[a] Fire brick, acid washed, 42/60 mesh was used as support. Concentration of liquid phase was 25%; liquid phase used was silicon rubber. The 5 ft preparatory column was ¾ in diam; the 10 ft column was ¼ in diam. Inlet pressure is given for individual cases; outlet pressure was not measured. The column temperatures are given in the text; the detector was maintained at 200 ma current. Thermal conductivity cells were used as detectors.

[b] Ten ft silicone rubber column, flow He, 20.0 psi, filament current 200 ma, sensitivity ×8.

[c] Impurity at 7.9 min as shoulder.

Acetylation of hydroxyl group increased the retention time, 1.0–1.3 min, a double bond decreased it from the original ester, 0.2–0.5 min in the hydroxy-stearates. In the oxo-stearates, a double bond increased the retention time, 0.4–0.8 min.

jected and the fraction corresponding to a retention time of 10 to 14 min was collected in ether solution. This procedure was repeated 17 times and the combined fractions were analyzed again by gas chromatography. A purity of 100% was shown on a 10-ft silicone rubber column with a retention time of 7.9 min at 239C, and on a Craig-succinate 10-ft column with a retention time of 26.9 min at 225C. It was recrystallized from methyl alcohol: mp 41.5–42C.

Methyl 2-hydroxystearate was synthesized from stearic acid through methyl 2-acetoxystearate according to Mendel and Coops (26). The methyl 2-hydroxystearate thus obtained gave one peak on gas chromatography. The retention time corresponded to methyl stearate, and did not show any retention time corresponding to methyl 2-hydroxystearate. An old silicone rubber column repeatedly failed to show retention of methyl 2-hydroxystearate. With a new 5-ft silicone rubber column, methyl 2-hydroxystearate appeared after 7.3 min at 228C. Methyl stearate appeared in 4.4-min at 231C. To remove the contaminant of methyl stearate, 7.0 g of the synthesized material was passed through a 5 x 35 cm activated silicic acid (Mallinckrodt) column, and developed with 800 ml Skellysolve F, 1750 ml of Skellysolve F and ether mixture (30:1), and 800 ml of Skellysolve F and ether mixture (20:1). Methyl stearate in the eluate was confirmed by gas chromatography. Elution was then continued with 1000 ml of a Skellysolve-ether mixture (20:1), 200 ml of a 10:1 mixture and 2150 ml of a 10:1 mixture. On removal of solvent from the last eluate a white residue was obtained which was recrystallized from methyl alcohol: water (10:1) yielding crystals: mp 65.5–66C.

2-Hydroxystearic acid. The methyl ester of 2-hydroxystearic acid was hydrolyzed in methanolic potassium hydroxide and recrystallized from chloroform yielding crystals: mp 90–91C.

2-Acetoxystearic acid. Four hundred twenty mg of 2-hydroxystearic acid was acetylated overnight with 3 ml acetic anhydride in 7 ml pyridine at room temperature. The reaction mixture was poured into ice water, allowed to stand overnight, extracted with ether, and the ether layer washed with water repeatedly. The ether was evaporated, and the white residue recrystallized from methanol to give crystals: mp 69–70C.

Methyl 2-oxostearate was obtained by the oxidation of methyl 2-hydroxystearate with chromium oxide at 37C according to the method of Bergstrom *et al.* (27) and was recrystallized from methyl alcohol: mp 54.5–55C.

Ethyl 3-oxostearate was synthesized from palmitoyl chloride and ethyl acetoacetate (28). It was recrystallized from ethanol (mp 37.5–38C). This oxostearate had the same retention time as methyl palmitate at 216C on a UCON-nonpolar, 5-ft. column; at 20.2 psi helium flow sensitivity 4×, after 16.8 min and at 226C on a 5-ft silicone rubber column; at 10.0 psi, sensitivity 1× after 5.0 min.

3-Oxostearic acid. The ethyl ester of 3-oxostearic acid was hydrolyzed with acetic acid, concentrated HCl for 48 hr (cf. 29,30), then shaken overnight and poured into ice water. The white precipitate was removed by filtration, washed with water, dried in vacuum, washed with Skellysolve B, and recrystallized from acetone, yielding colorless leaflets: mp 98.5–99C (decomp).

Me 12-hydroxystearate. Commercial 12-hydroxystearic acid (Nutritional Biochemical Corporation) was methylated and purified on a silicic acid column by means of chromatography and recrystallized from methyl alcohol: water (10:1) mp 57.5–58C.

12-Hydroxystearic acid. The ester of 12-hydroxystearic acid was hydrolyzed with methanolic KOH. Crystallization was stimulated by the addition of acetone: m.p. 81.5–82C.

12-Acetoxystearic acid. Four g of 12-hydroxystearic acid were refluxed with 4 g sodium acetate and 30 ml acetic anhydride for 12 hr, poured into 900 ml ice water, extracted with ether and Skellysolve F, and the extract washed repeatedly with water. The solvent was removed in vacuo; the residue was solid at −15C and liquid at room temperature. A portion was methylated with diazomethane and analyzed by gas chromatography which showed mainly one peak at 8.7 min. on a 10-ft silicone rubber column at 239C. It was then recrystallized from methyl alcohol at −15C yielding white needles which melted to a slightly yellowish oil at room temperature. Infrared analysis indicated no apparent free hydroxy groups. The oil was purified by passing it through a 2 x 22 cm, activated silicic acid column and developing with chloroform. It yielded white crystals: mp 29.5–31C.

Methyl 12-acetoxystearate. Seven and two tenths g of methyl 12-hydroxystearate were refluxed with 26 ml acetic anhydride and 3 g sodium acetate for 21.5 hr. The acetylated acid was purified by means of a silicic acid column. A colorless oil was obtained which showed one peak at 8.7 min by gas chromatography on a 10-ft silicone rubber column at 239C: mp 0.5–2C.

12-Oxostearic acid. Commercial 12-hydroxystearic acid (Nutritional Biochemical Corp.) was oxidized with sodium dichromate in acetic acid according to the method of Nichols *et al.* (13), then repeatedly recrystallized from methyl alcohol yielding white leaflets: mp 81.5–82C.

Methyl 12-oxostearate. 12-Oxostearic acid was methylated with 10% methanolic HCl or with diazomethane, purified by passing through alumina (Merck), eluted with acetone or ether, and recrystallized from a methyl alcohol: water mixture (ca. 15:1) yielding white leaflets: mp 46.5–47C, which showed one peak at 7.0 min on gas chromatography at 240C.

Methyl 10-oxostearate. 10-Oxostearic acid (courtesy Armour & Co.), mp 82–83C, was methylated and puri-

fied as previously reported for methyl 12-oxostearate, recrystallized from a methyl alcohol; water mixture (ca. 15:1) yielding white leaflets: mp 48–48C. This sample showed one peak at 6.7 min by gas chromatography on a 10-ft silicone rubber column at 240C.

Methyl 9-oxostearate was prepared from 9-oxostearic acid (courtesy Armour & Co.), m.p. 80.5–81.5C, and recrystallized from a methyl alcohol: water mixture (ca. 15:1), mp 49C. Retention time: 6.7 min on a 10-ft. silicone rubber column at 242C.

The methyl esters of the three oxostearates could not be separated from each other by gas chromatography.

Oxo-octadecenoic acid derivatives. 12-Oxo-*trans*-10-octadecenoic acid, mp 71–72C; 9,12-dioxo-*trans*-10-octadecenoic acid, mp 112–113C; 12-oxo-*cis*-9-octadecenoic acid, mp 89–90C; and methyl 12-oxo-*cis*-9-octadecenoate, a solid at −15C, were all prepared from castor oil (13).

Autoxidized 12-oxo-cis-9-octadecenoic acid. 12-Oxo-*cis*-9-octadecenoic acid was kept in an open bottle at room temperature for 30 days, then washed with Skellysolve F repeatedly. The insoluble residue was analyzed by IR.

Results and Discussion

Hydroxystearic acid derivatives. The carboxylic carbonyl absorptions of 2- and 12-hydroxystearic acid derivatives (Table II) were at positions normal to

TABLE II

Infrared Absorption Peaks in cm^{-1}
For Hydroxystearic Acids and Their Methyl Esters

Derivative	Alcoholic (ν O—H)	Carboxyl (ν C=O)	Ester (ν C=O)	Alcoholic (ν C—O)
2-OH-stearic acid	3520	1701	....	1149, 1086
12-OH-stearic acid	3300, 3195	1698	....	1131, 1078
Stearic acid	....	1698	....	....
Methyl 2-OH-stearate	3450	....	1722	1138, 1086
Methyl 12-OH-stearate	3320, 3230	....	1742	1137, 1087
Methyl stearate	....	....	1741	....

stearic acid (2) or 1701 and 1698 cm^{-1}, respectively. The ν O—H absorption of the alcoholic hydroxyl in the 2-hydroxy acid was located at 3520 cm^{-1}. However, the ester ν C=O absorption at 1722 cm^{-1} of 2-hydroxystearate showed a shift to a lower frequency. The ester absorption was usually at 1741 cm^{-1}. This shift occurred similarly in ν O—H absorption at 3450 cm^{-1} of 2-hydroxystearate. Both were considered to be the result of hydrogen bonding which appeared to be stronger in the ester than the acid (Fig. 1).

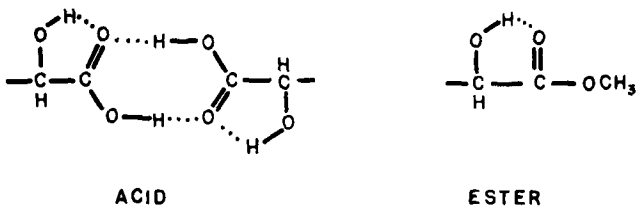

FIG. 1. Possible hydrogen bond in 2-hydroxy acid and ester and weak hydrogen bonds between 2-hydroxyl and carboxyl in acid.

In the ester formation of a dimer, absorption due to a conjugated dimer disappeared and a stronger intramolecular hydrogen bond arose. Jones (31) assigned the absorption of 2-hydroxystearic acid measured in crystalline films as follows: carbonyl showed absorption at 1745 cm^{-1}, a higher frequency than would be expected because it was in the 5-membered exocyclic system (Fig. 2) and ν O—H absorption occurred at

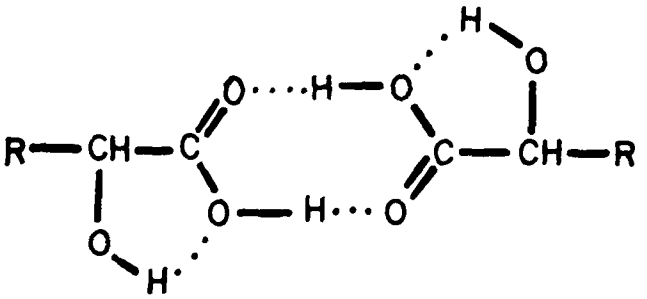

FIG. 2. Five-membered exocyclic system in 2-hydroxy acid proposed by Jones (31).

3440 cm^{-1} which was thought to be due to hydrogen bonding. These phenomena depended upon the state of measurement, but in Nujol mull no significant hydrogen bonded ν O—H absorption in 2-hydroxystearic acid was obtained. 12-Hydroxystearic acid showed broad ν O—H absorptions in 3300, 3195 cm^{-1}, which was apparently considered to be hydrogen bonded. According to the study of O'Connor *et al.* (14), ν O—H absorptions of 12-, and 10-hydroxystearic acids in the 3600 to 3000 cm^{-1} region were not obtained in chloroform solution, but ν O—H absorptions at 3610 and 3597 cm^{-1}, respectively, were obtained in both methyl esters due to strong intramolecular double bridge bonding (Fig. 3). The 12-hydroxystearic derivatives listed in

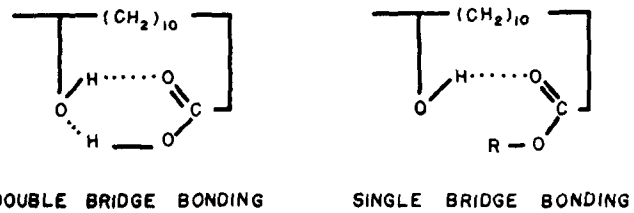

FIG. 3. Intramolecular bridge bonding of 12-hydroxystearic acid proposed by O'Connor *et al.* (14).

Table II show hydrogen bonded ν O—H absorptions in free acid and ester, and also unconjugated ester ν C=O absorption. Possibly in a crystal state there was some intermolecular bonding between alcoholic hydroxyls. This suggestion was supported by the fact that it was difficult to effect crystallization of 12-hydroxystearic acid as it gelled easily on crystallization, although with 10-hydroxystearic acid this was not the case (14). One might expect the existence of an intermolecular hydrogen bond, as postulated by O'Connor *et al.* (14), (Fig. 4). At least two kinds of hydrogen

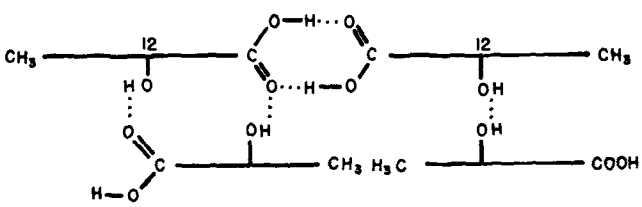

FIG. 4. Intermolecular hydrogen bond of 12-hydroxystearic acid postulated by O'Connor *et al.* (14).

bonded hydroxyls may exist; their absorption may be divided into two bands at 3300 cm^{-1} and 3195 cm^{-1}, respectively. The ν O—H absorption at 3610 and 3597 cm^{-1} of 12-hydroxystearate by O'Connor *et al.* (14) did not seem to be shifted to a lower frequency, although the absorption may be explained by single bridge bonding. Usually this bond band is at 3497 cm^{-1} (32).

Both 2- and 12-hydroxystearic acid derivatives had two strong absorption bands at approximately 1140 and 1080 cm^{-1}. These bands were assigned to the secondary alcoholic ν C—O of the saturated chain. 12-Hydroxystearic acid showed a shift to a lower frequency than other compounds, this absorption could also be ascribed to a strong intermolecular hydrogen bond.

By infrared analysis of 2-hydroxystearate a small contamination of stearate was distinguished. The presence of this contaminant was shown by the ester ν C=O absorption bands and by the nature of the gas chromatographic peaks.

2- and 12-Acetoxystearic acid derivatives. 2-Acetoxystearic acid had a carboxylic ν C=O absorption at 1724 cm^{-1} which was 23 cm^{-1} higher than 2-hydroxystearic acid at 1701 cm^{-1} and suggested the existence of a significant influence of the 2-acetoxy group on the carboxyl group (Table III). A similar effect caused

TABLE III

Infrared Absorption Peaks in cm^{-1}
For 2-, and 12-Acetoxystearic Acids and Their Methyl Esters

Derivative	Acetyl (ν C=O)	Ester (ν C=O)	Carboxylic (ν C=O)
2-Acetoxystearic acid	1761	....	1724
12-Acetoxystearic acid	1743	....	1714
Methyl 2-acetoxystearate	1766	1755	....
Methyl 12-acetoxystearate	1743	1743	....

the shift of ester ν C=O absorption to occur at higher frequency, 1755 cm^{-1}, in comparison with 2-hydroxystearate at 1722 cm^{-1}. These shifts to higher frequencies were similarly observed in acetyl ν C=O. Acetyl ν C=O absorption in both 2-acetoxystearic acid and its ester at 1761 cm^{-1} and 1766 cm^{-1} showed shifts to higher frequency than usual. 12-Acetoxystearate for example had acetyl ν C=O absorption at 1743 cm^{-1}. 12-Acetoxy-*trans*-9-octadecenoic acid and its methyl ester had unresolved acetyl ν C=O bands between 1739 and 1709 cm^{-1}. The acetate of elaidyl alcohol was formed at 1730 cm^{-1} and 12-acetoxy-*trans*-9-octadecenyl acetate at 1724 cm^{-1} (17). Between the free acid and ester, the ester group had a slightly stronger effect on the adjacent acetyl group than the free carboxyl group and was dependent on the dimeric form of the latter. These interactions of adjacent groups are well known in the steroidal ketone as Jones *et al.* (33) observed.

Oxo-stearic acid derivatives. Ketone, carboxylic, ester ν C=O absorptions were obtained separately in the usual position (Table IV). Absorption intensities of carboxylic and ester ν C=O (Fig. 5) showed

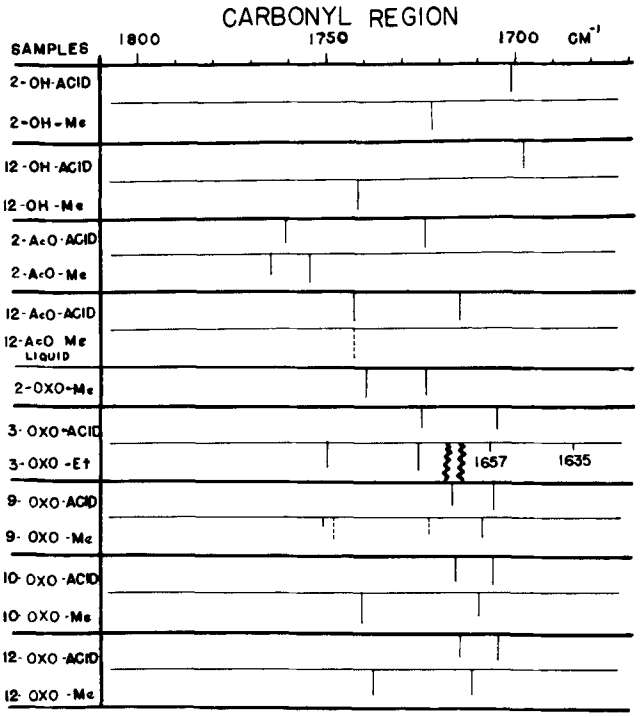

FIG. 5. Relative intensities in carbonyl region of oxygenated fatty acid derivatives.

stronger absorption than ketone, as previously cited (34).

The carboxylic δ O—H bands in oxostearic acids occurred at lower frequencies (about 50–60 cm^{-1}) than stearic acid (940 cm^{-1}). In a study of the infrared spectra of the polymorphism[3] of stearic acid, Jones *et al.* (2) obtained a remarkable difference of 48 cm^{-1} between the α-form and β-form. From this consideration, it appeared probable that the shifted δ O—H bands in oxostearic acids depended on the specific crystalline form which induced intermolecular influences. According to an infrared study of 4-oxostearic and 12-oxostearic acids in carbon tetrachloride solution by O'Connor *et al.* (12), carboxylic δ O—H bands occurred at 931 cm^{-1}. This study supported our results, similar bands were also obtained in chloroform solution.

In 2-oxo- and 3-oxostearate, ketonic absorption due to ν C=O of 1724, 1726 cm^{-1} was greater than was true of the other oxostearates. This might be due to the position of the ketone group in the long chain, that is, the proximity of the ketone to the carboxyl group. Other noteworthy band sequences were in the region between 1150 and 1100 cm^{-1} (Table V, A re-

TABLE IV

Infrared Absorption Peaks in cm^{-1}
For Oxo-stearic Acids and Their Methyl and Ethyl Esters

Derivative	Ester (ν C=O)	Carboxylic (ν C=O)	Ketone (ν C=O)	Carboxylic (δ O—H)
Methyl 2-oxostearate	1740	....	1724	....
3-Oxo-stearic acid	....	1705	1725, ...	915 (S. broad)
Ethyl 3-oxostearate	1750	....	1726, 1657[a] 1635[a]	....
9-Oxostearic acid	....	1706	1717	902 (W) 884 (S. broad)
Methyl 9-oxostearate	1748[b]	....	1723[b]	....[c]
10-Oxostearic acid	....	1706	1716	882 (S. broad)
Methyl 10-oxostearate	1741	....	1710	....[c]
12-Oxostearic acid	....	1705	1715	904 (W) 887 (S. broad)
Methyl 12-oxostearate	1738	....	1712	....[c]

[a] 1657 cm^{-1}: enolic hydrogen bonded ester ν C=O
1635 cm^{-1}: ν C=C of enol form
[b] Data had less reliability because of lack of adequate sample.
[c] Small bands occurred in this region, 10-oxostearate at 889, 868 cm^{-1}, 12-oxostearate at 890, 800 cm^{-1}, respectively, but these bands were obviously discriminated from carboxylic δ O—H absorption.

TABLE V

Infrared Absorption Peaks in cm^{-1}
For Oxo-stearic Acids and Their Methyl and Ethyl Esters

Derivative	A region	B region
Methyl 2-oxostearate	1131, 1110	1080, 1064, 1054, 1035, 1020, 995
3-Oxostearic acid	1131 (w), 1108	1086 (S), 1080 (S), 1047 unresolved
Ethyl 3-oxostearate[b]	1115[a]	1097, 1082,[a] 1040 (S)
9-Oxostearic acid	1135, 1114	Unresolved
Methyl 9-oxostearate	Unresolved	Unresolved 978
10-Oxostearic acid	1134, 1115	1091, 1075, ..., 1028, 1013
Methyl 10-oxostearate	1133, 1116	...., ..., 1031, 1017, ..., 969
12-Oxostearic acid	1131, 1117	1088, ..., 1058, 1033, 1004, 976
Methyl 12-oxostearate	1131, 1118	1085, 1061, ..., 1038, 995, 982

[a] Shoulder.
[b] Irregular absorptions because of its enol form.

[3] The crystal behavior of 17 homologous normal chain 3-oxo acids with 8 to 24 carbon atoms was studied by Stenhagen (35). The polymorphism of the mono-oxo- and monohydroxystearic acids were studied by Bergstrom (36) using thermal and X-ray methods. According to Bergstrom the hydroxy compounds were more complicated with regard to polymorphic behavior than the oxo compounds.

gion) and between 1100 and 950 cm^{-1} (Table V, B region).

Within the A region two weak but remarkable bands appeared which did not occur in 2-hydroxy-, 2-acetoxy-, 12-hydroxy-, and 12-acetoxystearic acid derivatives. Within the B region there were several weak, characteristic band sequences which could not be assigned. In 3-oxostearic derivatives, because of their enolic form, these two regions demonstrated spectra markedly different from other oxostearates. They had strong bands at 1040 cm^{-1} in the ester and at 1086, 1080 cm^{-1} in the acid which seemed due to ν C=O absorption of the enol form.

Band progressions occurring between the 1180 and 1350 cm^{-1} regions.[4] Hydroxystearic acid derivatives and acetoxystearic acid derivatives (Fig. 6) indicated bands similar to the progression bands of saturated acids. These bands arose from CH_2 wagging and/or twisting vibrations, especially in crystalline form. In oxostearic acids, these occurred with more irregularity due to some kind of molecular distortion which probably could be derived from the ketone group in a long chain. Progression irregularity, as in the case of tetrabromostearic acid (3) and unsaturated fatty acids (3,8), have been studied. Chain branching or the presence of a double bond tended to modify these patterns.

The strong absorption bands in the 1180–1350 cm^{-1} region were acetyl and ester ν C=O absorptions which apparently were discriminated from progression bands previously mentioned. The brackets showed acetyl ν C=O absorptions while dotted parentheses showed ester ν C=O absorptions (Fig. 6). Most of the ν C=O absorption was located in the 1170–1240 cm^{-1} region and covered some parts of band progressions. However, ester ν C—O absorptions in 2-oxostearate existed between 1250 and 1300 cm^{-1} which was at a higher frequency than usual. It seemed likely that this absorption was due to an adjacent ketone influence over ester ν C—O vibration as mentioned for 2-acetoxystearic acid derivatives.

3-Oxostearate had strong absorption at 1414 cm^{-1} which was ascribed to combined increments of δ C—H vibration of active methylenes at carbon atoms 1 and 4. This band was stronger than for other crystalline oxygenated fatty acid derivatives.

Unsaturated oxostearic acid derivatives. Absorption bands for 12-oxo-*trans*-10-, 9,12-dioxo-*trans*-10-octadecenoic acids coincided with data reported earlier (13) (Table VI). It seemed reasonable that a shift of *trans* δ C—H absorption to a higher position could be attributed to the influence of adjacent ketones. Very weak *cis* ν C=C absorption was obtained with 12-oxo-*cis*-9-octadecenoate. The autoxidation product of 12-oxo-*cis*-9-octadecenoic acid differed markedly from the starting material, especially in the ketone region which shifted from 1693 cm^{-1} to 1681 cm^{-1}, and in the *trans* δ C—H region where a new 1000 cm^{-1} strong band appeared. Both bands were specific in 9,12-dioxo-*trans*-10-octadecenoic acid as previously cited (13). Ellis *et al.* (37) proposed that autoxidized 12-oxo-*cis*-9-octadecenoic acid was 9,10-epoxy-12-oxo-octadecenoic acid, and King *et al.* (38) proposed a structure of 11,12-dioxo-*cis*-9-octadecenoic for this acid. The formula was finally established synthetically by Nichols who found one of the main autoxidized products to be 9,12-dioxo-*trans*-10-octadecenoic acid (13). Data in Table VI agreed with that found by Nichols *et al* (13). The epoxy groups, of which specific absorptions were at 847~833 cm^{-1} of *cis* [5] and at 893~877 cm^{-1} of *trans* (14,19), could not be found in our autoxidized sample by infrared analysis.

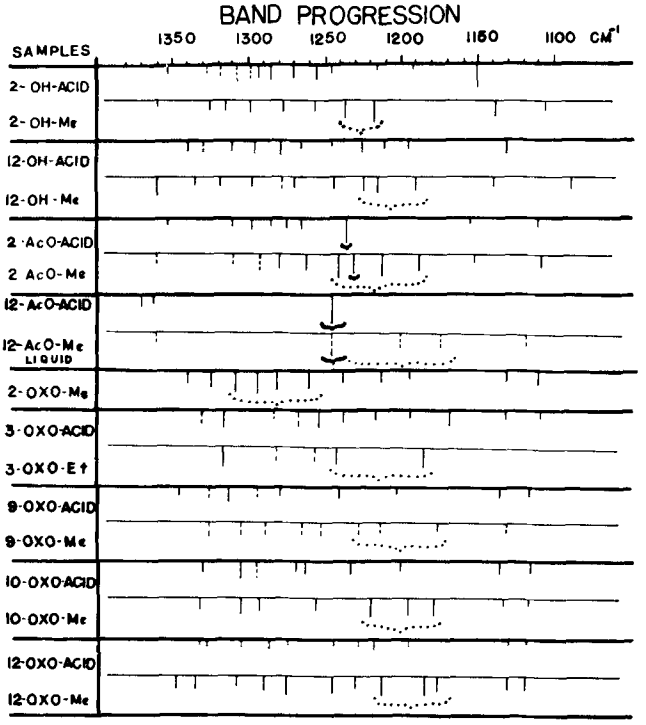

FIG. 6. Band progressions occurring between 1180 and 1350 cm^{-1}.

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[4] These band progressions were first proposed by Jones *et al.* (3).

[5] 9,10-Epoxystearic acid hydrazide, 846 cm^{-1} (in Nujol).

TABLE VI

Infrared Absorption Peaks in cm^{-1}
For Unsaturated Oxo-stearic Acid Derivatives

Derivative	Ester (ν C=O)	Carboxylic (ν C=O)	Ketonic (ν C=O)	C=C	δ C—H	Carboxylic δ O—H
12-Oxo-*trans*-10-octadecenoic acid	.....	1690	1690	1630(W)	978	930
9,12-Dioxo-*trans*-10-octadecenoic acid	.....	1700	1681	.....	1000[a]	935
12-Oxo-*cis*-9-octadecenoic acid	.....	1708	1693	.....	.....	947
Autoxidized 12-oxo-*cis*-9-octadecenoic acid	.....	1713	1681[b]	.....	1000[b]	940
Methyl 12-oxo-*cis*-9-octadecenoate	1746	.....	1723	1656(V.W.)	.....	.....

[a] *Trans* δ C—H were shifted to higher than usual frequency, for example, 12-oxo-*trans*-9-octadecenoic acid at 961 cm^{-1} (11).
[b] These bands suggested the existence of newly formed 9,12-dioxo-*trans*-10-octadecenoic acid in autoxidized 12-oxo-*cis*-9-octadecenoic acid.

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Flash Desolventizing Defatted Soybean Meals Washed with Aqueous Alcohols to Yield a High-Protein Product

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Abstract

A vapor-type desolventizer was developed previously at this laboratory to recover hexane and concentrated alcohols from soybean marcs. The work reported in this paper extends the application of this unit to the recovery of dilute alcohols. Soybean protein meals washed with aqueous alcohols are debittered to yield a better flavored product with a significant increase in protein content. The protein of defatted meal was increased from about 50 to 70 or 75% by washing with methanol, ethanol, or isopropyl alcohol in a concentration range of 50–70%. System modifications and critical variables were investigated so as to minimize residual alcohol and to yield a free-flowing homogeneous product. Residual alcohol in the desolventized flakes was 0.25–1.0%. Facility of removal followed the order—methanol, isopropyl alcohol, and ethanol. Two-stage flash desolventization as well as the use of the more dilute alcohols resulted in lower residual alcohol content of the desolventized product. After a minimum value for residual alcohol in the flakes is reached, further removal is difficult. However, water continues to be removed so that the alcohol/water ratio becomes higher with an increased vaporization force as with increased temperature. It is postulated that the alcohol is held by adsorption or hydrogen bonding. The desolventized products analyzed: protein 72–77%; Nitrogen Solubility Index 4–16; water absorption values 328–410%. The products were light-colored, granular, and free flowing. The soybean flakes extracted with methanol exhibited the best flavor.

A GROWING INTEREST in vegetable protein concentrates for foods has also increased interest in new methods for producing these concentrates. One method of increasing the protein concentration of soybean meal is to extract with dilute alcohols. This reduces the concentration of sugars and other alcohol-soluble compounds of the meal, thereby raising the protein content. The alcohols also remove a substantial amount of the beany flavor (1). Alcohol-water mixtures cannot be satisfactorily removed with conventional-type desolventizing equipment without adversely affecting the product. Such equipment degrades the protein through contact with hot metal surfaces during long retention periods. This produces such undesirable effects as moisture balling, scorching, denaturation, loss of bulkiness and poor moisture absorption properties which are undesirable in high-quality food products. A flash desolventizing unit, developed previously at this laboratory (2–4), permits extremely short retention time of meals in contact with high-temperature vapors.

This paper reports pilot-plant investigations on the recovery of aqueous alcohols from extracted soybean flakes by flash desolventizing. System modifications and critical variables affecting the degree of desolventization were evaluated, as well as changes in protein content, protein solubility, water absorption, and taste acceptance of the desolventized products.

Materials and Methods

Wet, defatted, soybean flakes extracted with methanol, ethanol, or isopropyl alcohol containing 30–50% water were furnished by a cooperating firm; but about half the runs were made on dry flakes rewetted with alcohol at the Northern Laboratory.

Moisture in the spent flakes was determined by the Karl Fischer method. Alcohol content was taken as the difference between the % total volatile and the % moisture. Total volatile was determined by oven drying in a Brabender moisture tester for 2 hr at 120C. Also, alcohol values in the desolventized flakes above 2% were determined by this procedure.

Small quantities of residual alcohol in the desolventized flakes were analyzed by a modified esterification procedure (5) for primary alcohols. Residual alcohol was extracted from the flake sample by refluxing with acetone in a Butt extraction apparatus. The boiling flask contained acetone and also phthalic anhydride to esterify the extracted alcohol in a reaction medium of pyridine.

Nitrogen Solubility Index (NSI) for the measurement of water-soluble protein was determined by a modified method of Smith and Circle (6) in which the water-solids mixture was agitated for 2 hr at 25C with flat-blade paddles at 125 rpm. NSI equals water soluble protein ÷ total protein × 100.

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