decyl and octadecyl sulfates. The unsaturated compounds and the dichloro compound are good wetting agents and lime soap dispersing agents, also excellent detergents in built solutions in hard water.

The ether alcohol sulfates whose properties were measured are chemical individuals [$R(OC_2H_4)_iOSO_3Na$, $i = 1, 2, 3, 4$] rather than a mixture of homologs [$R(OC_2H_4)_nOSO_3Na$]. The Krafft point, c.m.c., foam height, and detergency decreased with the number of ethenoxy groups; surface tension and wetting time increased. They are good emulsifying agents with excellent calcium stability, metallic ion stability, and lime soap dispersing power.

The triethanolammonium salts have much lower Krafft points than the sodium salts and a slightly lower c.m.c. They are much more soluble than the sodium salts but may form precipitates in the presence of large amounts of Na^+ or Ca^{++} ions. Their properties suggest a possible use as a component in shampoos or liquid detergents.

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Thermal Oxidation of Methyl Esters of Fatty Acids

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A REVIEW OF THE LITERATURE has shown that relatively little work has been done in a systematic and quantitative manner on the thermal oxidation of saturated fatty acid esters (1–12). In the present study, methyl esters of lauric, stearic, and oleic acids were oxidized in the presence of oxygen for various intervals of time. The decomposition products and the residual materials were subjected to chemical analysis in order to gain an insight into the mechanism of oxidation.

Experimental Procedures and Data

The methyl esters of lauric and stearic acids were prepared in this laboratory from technical high grade fatty acids.[2] The acids were twice crystallized from acetone (1 g./10 ml.), and the methyl esters were prepared from them by refluxing in absolute methanol, which had been saturated with hydrogen chloride gas (1 g./5 ml. methanol). The ester was fractionally distilled twice *in vacuo* in an all-glass apparatus, at 1 mm. of Hg. pressure. U.S.P. grade of oleic acid was crystallized twice from acetone (1 g./10 ml.) at −45°C. It was then kept at −15°C. over-night to remove traces of saturated fatty acids. Methyl oleate was prepared from oleic acid as described for the methyl esters of the saturated fatty acids. The analytical values of the pure methyl esters and the theoretical values are given in Table I.

To handle small quantities of the sample and to have maximum contact with bubbling oxygen, a fritted glass disk was fused into the side of a 125-ml. round-bottomed, glass-stoppered flask so that the disk nearly touched the bottom of the flask. In order to follow the oxidation of the esters and to insure trapping of condensible and noncondensible volatile products, the system shown in Figure 1 was devised. The reaction flask A was placed in the constant temperature bath F maintained at 200° ± 1°C. Tank oxygen was freed of moisture, carbon dioxide, and carbon monoxide by means of purification Train I. This train consisted of absorption tubes containing magnesium perchlorate and ascarite to remove moisture and carbon dioxide, a Vycor tube packed with copper oxide heated to red heat in order to convert carbon

TABLE I

Analysis of Methyl Esters of Fatty Acids, and Comparison with Theoretical Values

	Iodine value		Sap. value	
	Theory	Obtained	Theory	Obtained
Methyl laurate	0.00	0.03 0.00	261.8	262.2 261.4
Methyl stearate	0.00	0.18 0.15	188.0	187.8 187.3
Methyl oleate	85.65	85.16 84.74	189.2	189.3 189.8

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[2] Obtained through the courtesy of Armour and Company, Chicago, Ill.

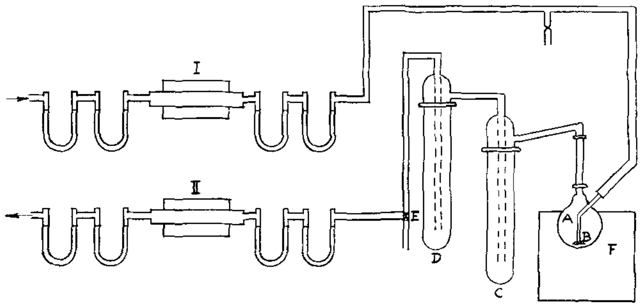


FIG. 1. Apparatus for thermal oxidation.

monoxide to carbon dioxide and hydrogen to water, and absorption tubes of magnesium perchlorate and ascarite to absorb the carbon dioxide and water thus formed. Absorption Train II was set up in the same manner as above, and all the tubes in Train II were accurately weighed. With this system it was possible to calculate the amounts of carbon dioxide, carbon monoxide, and hydrogen formed during the oxidation. All the connections in this apparatus were standard or ball-type, ground glass joints, except for a small piece of Tygon tubing connecting the oxygen tank with the thermal oxidation flask.

The procedure followed for oxidation of the methyl esters was as follows. The Vycor tubes which contained copper oxide were heated to dull red, and the oil bath was brought to a temperature of 200°C. The two traps C and D were filled with a dry ice-trichloroethylene mixture to maintain a steady −80°C. The reaction flask was weighed, approximately 50 g. of the ester were accurately weighed into it, and the flask was placed in the oil bath. The flask was connected to the oxygen inlet and the cold traps. Stopcock E was turned so that the oxygen bubbling through the ester flushed away the air in the system. After one minute of flushing the stopcock was turned to connect the cold traps to Absorption System II. The flow rate through the mineral oil bubbling column at the end of Absorption Train II was checked, and the amount of oxygen flowing from the tank was controlled to yield 150 bubbles per minute. This was determined to be equivalent to 300 ml. per minute.

At intervals of 1, 2, 4, 8, and 16 hrs. the air condenser attached to the thermal oxidation flask and the traps from the −80°C. bath were removed. They were washed with absolute methanol, the washings were collected in a 250-ml. volumetric flask and diluted to volume. Aliquots of this methanolic solution were used for further analysis.

Twenty-five ml. of the methanolic solution which contained the condensible vapor phase were neutralized with 0.1 N sodium hydroxide, and this solution was then extracted three times with 15 ml. of ethyl ether. Twenty ml. of 2,4-dinitrophenyl hydrazine reagent prepared in carbonyl-free absolute methanol were then added to the ether solution, the ether was allowed to evaporate slowly and the volume of the methanolic solution was reduced to 5 ml. under vacuum. After the addition of distilled water in small quantities the slightly turbid solution was cooled over-night in the refrigerator to allow the 2,4-dinitrophenyl hydrazones to separate. These were filtered off and dissolved in carbonyl-free methanol; the solution was chromatographed on Whatman No. 1 paper which had been sprayed with a mixture of 20% propylene glycol and 80% methanol and air-dried for 8 hrs. at room temperature.

The method of Ellis, Gaddis, and Currie, with some modifications gave satisfactory, though not efficient, resolution of the 2,4-dinitrophenyl hydrazones (13). Heptane which had been saturated with methanol was used as the solvent system. Standards were run simultaneously to help in the identification of the spots.

The fatty acids in the condensible vapor phase were converted to their hydroxamate derivatives (14) and chromatographed on Whatman No. 1 paper, with butanol saturated with water as the solvent system. Standards were run simultaneously, and a 4% solution of ferric chloride in absolute methanol was used as the chromogenic reagent.

The infrared absorption on all the original and thermally oxidized samples was run on a Perkin-Elmer Model 21 recording spectrophotometer, using a 10% solution of the sample in chloroform. The acid value, saponification value, and Wijs iodine value were determined by the official method of the American Oil Chemists' Society except that a smaller sample was used (15). The ester value was determined as the difference between the saponification and free fatty acid values. The acetyl chloride-pyridine method of Smith and Shriner was used in the determination of the hydroxyl groups (16), a correction was applied to the individual samples for their free fatty acid content.

A modification of the method of Bryant and Smith gave satisfactory results in the determination of the carbonyl groups in the thermally oxidized esters (17). Titration of the released hydrochloric acid was conducted with the help of a pH meter, taking the endpoint at pH 4.6. To determine the oxygen content of the samples, carbon and hydrogen analyses were performed and the oxygen content was calculated by differences.

Results and Discussion

The thermal oxidation of pure methyl esters at 200°C. led to the formation of products which differed both physically and chemically from the pure esters. Methyl stearate which was solid at room temperature turned into a yellowish liquid at the end of 4 hrs. All the esters turned into dark viscous products at the end of 16 hrs.

A loss in weight of the esters and a gain in weight of the absorption tubes were noted (Table II). The loss in weight has been calculated both in percentage and as grams per mole. The noncondensible decomposition products, namely carbon dioxide, carbon monoxide, and hydrogen, have been calculated on a weight and molar basis. The amounts of carbon monoxide and hydrogen have been calculated as equivalent to the carbon dioxide and water collected in the absorption tubes. The evolution of hydrogen indicated that dehydrogenation of the ester molecules occurred. The increased release of carbon monoxide in the earlier stages and that of carbon dioxide in the later stages of thermal oxidation indicate that more carbonyl compounds are formed and decomposed during the earlier than the later stages of oxidation and that these carbonyl compounds are the precursors of the carbonyl compounds which on further decomposition formed carbon dioxide. The evolution of carbon mon-

TABLE II

Thermal Oxidation of Methyl Esters

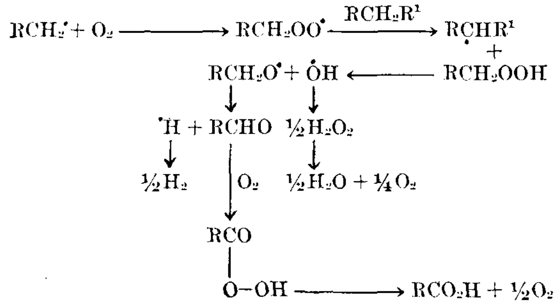
Sample	Time	Wt. of sample	Loss in wt.	Loss	Grams per molar grams of ester				Molar grams per molar grams of ester		
					Loss	CO_2	CO	H_2	CO_2	CO	H_2
	hrs.	*g.*	*g.*	%							
Methyl laurate	0	49.03	......	......	......	......	......	......	......	......	......
	1	39.23	1.18	2.42	5.18	1.57	2.13	0.03	0.04	0.08	0.015
	2	29.27	1.50	6.24	13.38	4.29	4.92	0.09	0.10	0.18	0.045
	4	19.45	2.19	13.74	29.44	11.73	10.73	0.40	0.27	0.38	0.200
	8	9.56	1.94	23.71	50.81	23.38	16.16	0.87	0.53	0.58	0.435
	16	8.24	1.32	37.51	80.39	38.60	21.83	1.10	0.88	0.78	0.550
Methyl stearate	0	52.59	......	......	......	......	......	......	......	......	......
	1	43.73	0.96	1.82	5.44	1.11	1.69	0.09	0.03	0.06	0.045
	2	34.40	1.69	5.70	17.01	3.33	4.26	0.19	0.08	0.15	0.095
	4	24.22	2.10	11.80	35.21	10.27	11.41	0.47	0.23	0.41	0.235
	8	13.91	2.60	22.52	67.20	22.55	19.85	0.80	0.51	0.71	0.400
	16	10.51	3.41	46.99	140.24	37.33	24.69	1.06	0.85	0.88	0.530
Methyl oleate	0	51.95	......	......	......	......	......	......	......	......	......
	½	42.77	0.40	0.76	2.27	0.37	0.51	0.02	0.01	0.02	0.010
	1	42.20	1.63	2.09	6.20	1.17	1.29	0.06	0.03	0.05	0.030
	2	31.80	0.57	5.94	17.62	3.02	3.23	0.12	0.07	0.12	0.060
	4	21.19	1.80	11.59	34.37	8.13	6.82	0.23	0.18	0.24	0.115
	8	10.10	2.44	23.12	68.54	17.84	11.00	0.35	0.41	0.39	0.175
	16	8.98	1.12	34.21	102.10	29.87	14.27	0.46	0.68	0.51	0.230

oxide could have occurred by the elimination of a carbonyl group from compounds containing the groups —COCOCOR and —$COCH_2COCO_2R$. Acids of the type $HO_2C–CH_2CO_2CH_3$ containing active methylene groups lose carbon dioxide readily when heated. Possible formation of acyl radicals and their decomposition to form carbon monoxide might also be the mechanism involved.

The condensible volatile products consisted of an aqueous and an oily layer. Paper chromatography of the hydroxamates of the fatty acids in the condensible decomposition products showed the following. a) In the oxidation products of methyl laurate the presence of propionic, valeric, and nonanoic acids was proven. Acetic acid was detected at the end of 4 hrs., which indicated that acetic acid was a secondary product. b) Oxidation products of methyl stearate were nonanoic acid at the end of 1 hr.; acetic, propionic, butyric, valeric, and nonanoic acids at the end of 4 hrs.; and acetic, caproic, and caprylic acids at the end of 16 hrs. Here also the lower fatty acids were recognizable as secondary products of the initial breakdown products. The presence of nonanoic acid at the end of 1 hr. indicated that the C–C linkage between 9 and 10 carbons is very susceptible to oxygen attack at the higher temperatures. c) The oxidation products of methyl oleate contained a variety of fatty acids, particularly nonanoic acid, even after oxidation for 1 hr., indicating thereby oxygen attack at the double bond. Acetic acid was noticed at the end of 16 hrs.

Paper chromatography of the 2,4-dinitrophenyl hydrazones of the carbonyl compounds in the condensible decomposition products showed the following. a) The oxidation products from methyl laurate contained butyraldehyde, 4-heptanone, and nonylaldehyde. Acetaldehyde was detected at the end of 16 hrs. proving this to be a secondary oxidation product. b) The presence of acetaldehyde, propionaldehyde, *n*-hexanal, and nonylaldehyde was detected in the oxidation products from methyl stearate. c) The oxidation products of methyl oleate contained butyraldehyde and nonylaldehyde. The presence of the latter at the end of 1 hr. indicated chain scission of the double bond by oxygen attack.

The mechanism postulated by Fritsch and Deatherage for the autoxidation of methyl oleate seems applicable for the formation of water, fatty acids, and hydrogen (18). Schematically the reactions involved are:



The increase in the acid value as the thermal oxidation progressed indicated scission of the ester chain to form free fatty acids and lower molecular weight esters (Table III). The increase in ester value may be caused by this scission or by the formation of new ester linkages. This increase could also result from the formation of lactones, the presence of which has been established by their specific absorption bands in the infrared spectra.

The apparent iodine values of thermally oxidized methyl laurate and methyl stearate indicated the presence of unsaturation in the molecules (Table III). Part of the apparent iodine value could be caused by the presence of carbonyl compounds. In the present study, thermally oxidized methyl stearate was reduced with lithium aluminum hydride in the conventional manner, and the Wijs iodine value was determined on the reduced sample. The iodine number changed from 13.13 to 9.45, thus establishing the presence of unsaturation in the molecule. Even though methyl oleate also released hydrogen during thermal oxidation, it showed a decreased iodine value as the oxidation progressed. This could be on account of a more rapid polymerization as evidenced by the nearly solid product obtained at the end of 16 hrs. of oxidation.

The total percentage of oxygen was calculated from the functional group analysis of the esters (Table III). This value was found to be in close proximity to the percentage of oxygen as calculated from carbon hydrogen analysis. Although methyl stearate and its thermally oxidized samples showed a wider margin of difference than those from methyl laurate or methyl

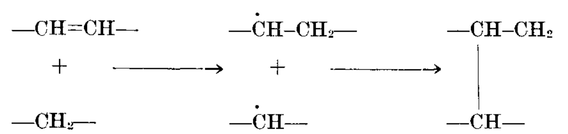
TABLE III

Analysis of the Thermally Oxidized Esters

Sample	Time	I.V.	% Oxygen of groups				Total	% O_2 from C-H analysis
			(COOH)	(CO_2CH_3)	(C=O)	(OH)		
	hrs.							
Methyl laurate	0	0.03	0.00	14.96	0.00	0.00	14.96	14.95
	1	2.06	0.75	14.87	0.54	0.98	17.14	15.99
	2	4.50	1.76	15.07	0.82	1.24	18.91	18.46
	4	8.46	3.24	16.07	0.99	1.42	21.71	22.52
	8	9.16	4.79	17.55	1.26	2.01	25.62	26.02
	16	10.09	8.03	18.99	2.43	2.55	31.99	29.10
Methyl stearate	0	0.18	0.00	10.72	0.00	0.00	10.72	10.13
	1	2.51	0.84	10.83	0.69	0.84	13.20	12.32
	2	5.21	1.63	10.98	1.18	1.17	14.97	13.49
	4	10.08	2.59	11.69	2.07	1.87	18.22	16.48
	8	11.89	4.14	14.10	2.40	2.68	23.32	20.25
	16	13.13	6.33	17.62	3.02	3.40	30.38	24.27
Methyl oleate	0	85.16	0.00	10.80	0.00	0.00	10.80	11.00
	½	69.20	0.29	11.27	0.41	0.70	12.67	13.41
	2	45.29	0.82	12.11	0.44	2.27	15.63	15.67
	4	30.82	1.52	13.95	0.95	1.91	18.33	19.07
	8	21.68	2.31	16.59	1.36	1.86	22.12	21.82
	16	16.23	3.08	18.04	1.77	1.67	24.56	24.88

oleate, no oxygen could be present which had not been detected as functional groups. On this basis it can be postulated that polymerization had taken place through ester linkages or carbon-carbon linkages.

Deatherage and Mattill have established the presence of esters upon autoxidation of oleic acid (19). As opposed to this theory, Sunderland has proposed another mechanism in which a carbon-carbon double bond in a molecule abstracted a hydrogen atom from a methylene group in another molecule and then joined the methylene group to the double bond to give a carbon-carbon bond between the two molecules (20):



$$\begin{array}{ccccc} \text{—CH=CH—} & & \text{—}\dot{\text{C}}\text{H-CH}_2\text{—} & & \text{—CH-CH}_2 \\ + & \longrightarrow & + & \longrightarrow & \vert \\ \text{—CH}_2\text{—} & & \text{—}\dot{\text{C}}\text{H—} & & \text{—CH—} \end{array}$$

In agreement with the findings of Nobori (21) it was shown in the present study that methyl stearate was more susceptible to oxygen attack than methyl laurate (Table II). The partial polymerization that had occurred in the stearate and laurate was caused by the double bonds that are formed during thermal oxidation. The low decomposition rate of methyl oleate may have been attributable to a more rapid polymerization (Table II). This polymerization occurred possibly through free radical systems formed during the oxidation.

From these considerations the chemistry of thermal oxidation in the early stages of the reaction may consist of three fundamental steps: hydroperoxide formation; formation of intermediates containing hydroxyl, carbonyl, and carboxyl groups; and association of intermediates to form higher-molecular-weight compounds. By application of this hypothesis the initial oxygen attack of methyl oleate resulted in the formation of a hydroperoxide, which decomposed almost instantaneously at the high temperature to generate free radicals. There may be some free hydroxyl radicals formed during this reaction, as has been shown earlier. Any or all of these free radicals may be present at any one instant in any of their possible resonance structures. These various free radicals may then react among themselves to form complex polymeric materials. Chain transfer and chain termination could be accomplished by combination with another large free radical, or by abstraction of a hydrogen atom from a molecule or by reaction with a free hydroxy radical. The isolation of dihydroxy stearic acid from thermally oxidized corn oil by Perkins (22) definitely indicates that free hydroxy radicals are formed at high temperatures and that they react with double bonds.

A hypothetical outline (Figure 2) illustrates a possible mechanism of thermal oxidation of methyl oleate and the formation of polymers and volatile products. With esters of saturated fatty acids the attack of oxygen at high temperatures causes dehydrogenation and thus unsaturation in the molecule. After formation of double bonds, further degradation and polymerization of these molecules proceeds in a manner similar to that proposed for methyl oleate.

Summary and Conclusions

Methyl esters of lauric, stearic, and oleic acids were thermally oxidized at 200°C. in the presence of oxygen for varying intervals of time. The loss in weight of the ester and the amounts of the volatile noncondensible phase in terms of carbon dioxide, carbon monoxide, and hydrogen were measured. The condensible vapor phase was analyzed and found to con-

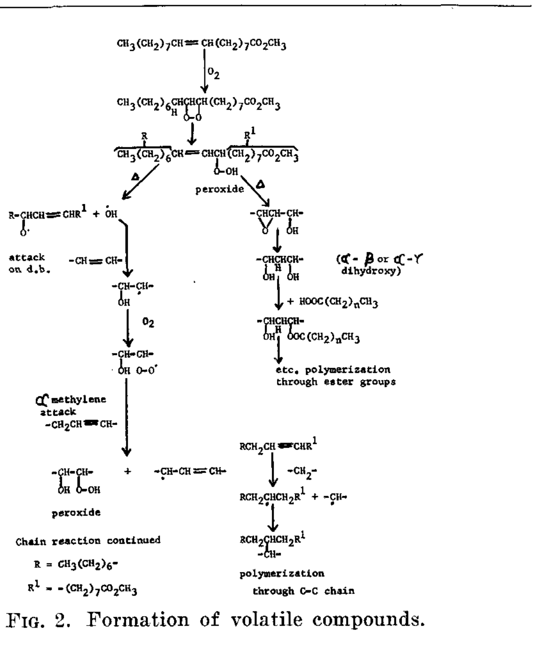


FIG. 2. Formation of volatile compounds.

tain a variety of carbonyl and carboxyl compounds, indicating a random oxygen attack of the ester molecule. The ester was analyzed for carboxyl, ester, carbonyl, and hydroxyl groups and for unsaturation. Increased chain length showed increased susceptibility to oxidation. From the analytical values and the decomposition products a possible mechanism of thermal oxidation through a free radical system has been proposed. Unsaturation; hydroperoxide formation; instantaneous decomposition of the hydroperoxide to form various hydroxy, carbonyl, and carboxyl compounds; decomposition of these compounds to release carbon dioxide, carbon monoxide, and water; and polymerization through either carbon-carbon linkages or ester linkages have been suggested as a possible mechanism of thermal oxidation of fatty acid esters.

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The Relationship of Corn Oil and Animal Fats to Serum Cholesterol Values at Various Dietary Protein Levels[1, 2]

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THE NEED for a high fat, high cholesterol diet for the development of hypercholesteremia in a reasonable period of time has been recognized in many previous studies (1). In fact, these studies have been interpreted to indicate that a low fat, low cholesterol diet may serve as the best means of preventing hypercholesteremia (2, 3). An over-emphasis on dietary fat may have prevented consideration of other dietary components such as protein (4, 5). It would seem that a high fat diet would automatically lower protein intake as total food consumption would decrease. Furthermore, in experimental studies on the dietary factors which influence serum cholesterol levels, added fats and oils such as butter, margarine, and corn oil rather than whole milk, eggs, and meat have served as dietary sources of fat. The added fats upset dietary fat to protein ratios more than food items which contain both fat and protein. It would seem therefore that comparisons in diet in which only the fat is varied may yield misleading results or may be difficult to interpret.

In previous studies (6) we have attempted to correlate the fat and protein and the total metabolizable energy to the protein or E/P ratio of the diet with changes in carcass and serum cholesterol levels. In this presentation we have used previous studies as a means of introducing new data on the relationship of corn oil and animal fats to serum cholesterol levels.

Methods

In most of our studies, groups of chicks (New Hampshire Columbian Cross) were kept in three replicates of 10 birds each, on a nutritionally complete basal diet (Table I). The various experimental diets listed in Tables II, IV, and VI were modifications of the basal diet shown in Table I. The fat and protein levels of these diets were adjusted at the expense of Cerelose. The basal diet furnished all of the known amino acid, vitamin, and mineral requirements of the chick. The birds were weighed at weekly intervals, and the experiments were terminated after three to four weeks. Five ml. of blood from the two median weight chicks in each replicate were obtained *via* heart puncture, and in some treatments the weighed individual carcasses were digested with concentrated hydrochloric acid (1 ml./g. tissue) at 50°C. for 24

TABLE I

Composition of the Basal Diet

Ingredients	Percentage
Cerelose	57.11
Dracket assay protein	35.30
DL-Methionine	0.75
Glycine	0.30
Glista salts[a]	5.34
Choline chloride	0.20
Corn oil	1.00
Vitamins	+
Total	100.00

[a] (11) 0.88% NaCl, 0.002% $ZnCl_2$ 0.002% $CuSO_4 \cdot 5H_2O$, 0.0009% H_3BO_3, 0.0001% $CoSO_4 \cdot 7H_2O$, 0.004% KI, 0.14% Fe Citrate, 0.25% $MgSO_4 \cdot 7H_2O$, 0.90% K_2HPO_4, 0.065% $MnSO_4 \cdot H_2O$, 0.30% $CaCO_3$, 2.80% $Ca_3(PO_4)_2$.

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[2] Portion of a thesis to be presented by M. G. Kokatnur as partial fulfillment of the requirements for the degree of Doctor of Philosophy in Food Technology.