CXXX.—*The Distribution of Saturated and Unsaturated Higher Fatty Acids in Mixed Synthetic Glycol Esters.*

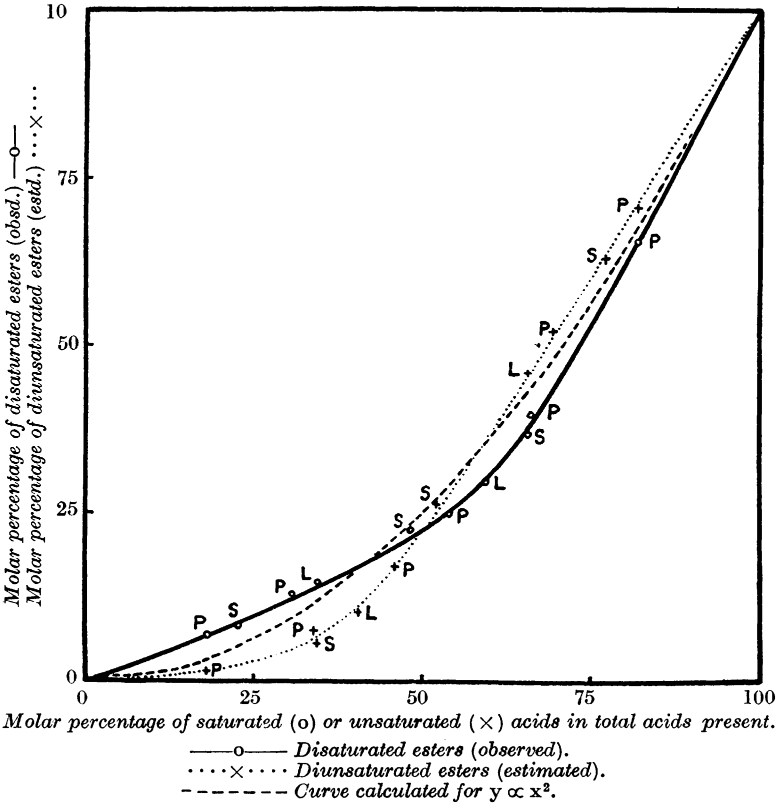
By RAMKANTA BHATTACHARYA and THOMAS PERCY HILDITCH.

WE have recently demonstrated (*Proc. Roy. Soc.*, 1930, *A*, **129**, 468) that, when synthetic glycerides are prepared from mixtures of higher fatty acids containing varying proportions of saturated and unsaturated acids, the fully saturated glyceride contents of the synthetic fats lie on a smooth curve when plotted against the molar percentage of saturated fatty acids present in their mixed fatty acids. This curve is not very dissimilar from, although not identical with, that calculated on the assumption that the content of fully saturated glycerides is proportional to the cube of the molar concentration of saturated fatty acids in the mixed acids, *i.e.*, on the assumption that molecules of fatty acid are combined, according to their relative concentrations, indiscriminately three at a time with the molecules of glycerol. More interesting is the circumstance that the corresponding values for all animal fats (including milk and body fats) and vegetable " pericarp " fats so far examined give points on the graph lying close to and roughly parallel, though not coincident, with the curve for the synthetic glycerides. Animal fats contain as a rule somewhat more, and " pericarp " fats somewhat less, fully saturated glycerides than the synthetic fats with the same ratio of saturated to unsaturated acids. The contrast in glyceride structure between all these classes and vegetable-seed fats is profound, for in the latter the determining factor is a tendency towards " even distribution " of the fatty acids amongst the glycerol molecules, and fully saturated glycerides rarely appear in appreciable amounts until the molar proportion of saturated acids in the mixed fatty acids reaches about 60%.

The presence of three replaceable hydroxyl groups in the glycerol molecule adds considerably to the complexity of the products obtained during their esterification, and we have therefore carried out a similar investigation on the same general lines with ethylene glycol substituted for glycerol. Unfortunately, since natural glycol esters of the higher fatty acids are not known, no comparison of the synthetic with the natural products can be made in this series; but on the other hand, the possible combinations are merely those of disaturated, diunsaturated, or monosaturated–monounsaturated esters, whereas in the glycerides it is evident that, in addition to simple trisaturated or triunsaturated esters, there are possibilities of two isomeric forms of both monosaturated–diunsaturated and disaturated–monounsaturated glycerides. This refers, of course, to cases (such as those we have chosen) where only one saturated and one unsaturated acid are present, the number of possible individual esters being greatly increased when mixtures of several saturated and of several unsaturated acids are considered.

Lauric, palmitic, or stearic acid was mixed in various amounts with the unsaturated acids of olive oil (88% oleic and 12% linoleic

FIG. 1.



acid), and the individual mixtures of acids were converted into glycol di-acid esters. The proportions of saturated and unsaturated acids in the esters obtained were estimated from their iodine absorption (it was found, as in the corresponding synthetic glycerides, that palmitic, stearic, and oleic acids were esterified at much the same rates, but that lauric acid reacted more rapidly with glycol than did oleic acid). Weighed amounts of the esters were oxidised in acetone solution with anhydrous potassium permanganate and the completely saturated glycol esters (the only neutral compounds present, all unsaturated esters having been converted into acidic compounds during the oxidation) were recovered, weighed, and examined; the values so obtained may be taken as accurate to the nearest unit per cent. The general results obtained are shown in Table I and Fig. 1.

TABLE I.

Composition of mixed synthetic glycol esters.

[S_2 = Disaturated esters; S_1U_1 = monosaturated–monounsaturated esters; U_2 = diunsaturated esters.]

Saturated I.	Total acids present, mols. %.		S_2-Esters, %,		S_1U_1-Esters (estd.), mols., %.	U_2-Esters (estd.), mols., %.
	Satd. II.	Unsatd. III.	By wt. IV.	By mols. V.	VI.	VII.
Lauric	34·4	65·6	11·6	14·5	39·8	45·7
,,	59·6	40·4	25·5	29·4	60·4	10·2
Palmitic	18·2	81·8	6·3	6·9	22·6	70·5
,,	30·5	69·5	12·0	12·8	35·4	51·8
,,	53·9	46·1	23·7	24·8	58·2	17·0
,,	66·1	33·9	38·3	39·6	53·0	7·4
,,	82·0	18·0	64·2	65·3	33·4	1·3
Stearic	22·7	77·3	8·1	8·1	29·2	62·7
,,	48·0	52·0	22·6	22·6	50·8	26·6
,,	65·5	34·5	36·4	36·4	58·2	5·4

The molar proportions of monosaturated–monounsaturated glycol esters (VI), and, in turn, those of the diunsaturated esters (VII), can be deduced from the molar percentages of disaturated ester (V) and of the total saturated acids (II) present in each case; a small error in the determination of either of the latter values will, however, lead to disproportionately larger errors in these results, especially in the data for diunsaturated esters (VII), when these involve a comparatively small numerical difference between two large experimentally determined figures.

Fig. 1 illustrates (i) the molar percentages of disaturated esters (V) plotted against the total molar percentage of combined saturated acids (II) (full curve); (ii) the estimated approximate molar percentages of diunsaturated esters (VII) plotted against the total molar percentage of combined unsaturated acids (III) (dotted curve); (iii) the curve (broken) representing the state of affairs if the molar proportions of disaturated esters were proportional to the square of the molar concentration of saturated acids in the mixed acids.

The observed molar proportions of disaturated esters (V) lie on a smooth curve, irrespective of whether the saturated acid is lauric, palmitic, or stearic; the deduced figures for diunsaturated esters (VII) also lie on a more or less smooth curve. For equimolecular amounts of saturated and unsaturated acids combined in the mixed synthetic ester, these curves intersect at a point indicating about 22 mols.% each of disaturated and diunsaturated ester, and about 56 mols.% of mixed esters containing both saturated and unsaturated acids.

If, in the esterification, the fatty acid molecules were combined with glycol molecules indiscriminately two at a time according to their relative numbers, the molar amount of disaturated esters being then proportional to the square of that of the saturated acids in the mixture (broken curve, Fig. 1), the composition would be 25 mols.% of disaturated and of diunsaturated ester, and 50 mols.% of mixed ester for equal total amounts of saturated and unsaturated acids. The experimental and " calculated " curves intersect at a point corresponding with the presence of 45 mols. of saturated and 55 mols. of unsaturated acids in the mixed synthetic ester, whereas the corresponding point of intersection for the synthetic glycerides (*loc. cit.*) coincided with equimolecular proportions of combined saturated and unsaturated acids.

Thus, broadly speaking, there is a tendency both in the glycol and the glycerol series for esterification to take place according to the probable chances of combination of molecules of saturated and unsaturated acids as determined by the relative numbers of each present; but, when the saturated acids are in excess of the unsaturated, the observed amount of fully saturated esters is somewhat less than that calculated as described, whilst the reverse holds for esters which contain an excess of unsaturated over saturated acids. This parallelism, and also the divergences mentioned, between the fully saturated esters present in each group (glycol and glycerol) and the respective values for the " calculated " curves (*i.e.*, y proportional respectively to x^2 and to x^3), is illustrated in Table II, which gives, from the respective graphs, the molar percentages of fully saturated esters which correspond with total molar concentrations of 20—80% of saturated acids in the synthetic products.

TABLE II.

Total mols. saturated acid present, %.	Glycol di-esters.		Triglycerides.	
	$y \propto x^2$ curve.	Exptl. curve.	$y \propto x^3$ curve.	Exptl. curve.
20	4	7·5	1	2·5
30	9	12	3	5
40	16	17	6·5	8
50	25	22·5	12·5	12·5
60	36	31·5	21·5	18·5
70	49	45	34·5	30
80	64	62	51	47·5

There may possibly be a difference in behaviour between the glycol and glycerol esters when mixtures containing high proportions of saturated acids are esterified; the unsymmetrical nature of the graph connecting the proportion of diunsaturated glycol esters with the total content of unsaturated acids appears to indicate something of this nature, and moreover, with mixtures of lauric and oleic acid containing more than 75 mols.% of the former (which esterifies definitely more rapidly than oleic acid), it has appeared that little or no diunsaturated ester occurred in the products. Hitherto, no evidence has been given to show that the mode of assemblage of oleic acid into esters of glycol or glycerol differs from that of the saturated acids; and we feel that any discussion of this feature must be reserved until it has received further investigation.

EXPERIMENTAL.

The ethylene glycol was a redistilled fraction (b. p. 194—195°) from synthetic glycol provided by the British Dyestuffs Corporation. The unsaturated fatty acids were obtained from olive oil acids by removing the saturated acids in the form of alcohol-insoluble lead salts; the acids employed had an iodine absorption of 100·8%, corresponding with a composition of 88% oleic and 12% linoleic acid. Lauric, palmitic, and stearic acids were prepared from methyl esters rich in these components (accumulated in the course of analysis of various oils in this laboratory); the respective ester concentrates were refractionated and fractions of pure methyl laurate and palmitate, and of methyl stearate containing about 6% of oleate, were obtained and converted into the corresponding acids.

The esterification of fatty acid mixtures with glycol was carried out, with a few modifications occasioned by the lower boiling point of glycol as compared with glycerol, in the same way as in the case of the glycerol esters (*loc. cit.*). Thus it was found convenient to take the calculated amount of glycol required by theory in order to get the maximum yield, and somewhat lower temperatures and higher pressures were employed in the early stages of esterification in order to lessen loss of free glycol by evaporation. Some details of a particular case will serve to illustrate the general procedure :—

Palmitic acid (38·4 g.) and unsaturated acids (42·3 g.) were heated with glycol (9·2 g.) and naphthalene-β-sulphonic acid (0·4 g.) under an air-condenser at about 100° for an hour at ordinary pressure, whilst during the second hour the vacuum of a water-pump was employed and the temperature was raised slowly to 135°; heating under vacuum was then continued at 135° for a further 2 hours. The glycol esters were separated from unchanged fatty acids and finally dried at 100° under reduced pressure, the yield being 75 g. (iodine absorption, 46·6%; saponification equiv., 281·4). The substantial absence of glycol mono-esters in the products is indicated by their saponification equivalents.

The various mixed esters thus prepared are described in Table III.

TABLE III.

Glycol di-esters synthesised.

Saturated acid.	Proportion used in esterification, mols. %.	Glycol esters obtained. M. p.	I.V., %.	Sap. equiv.	Saturated acid content, mols. %.
Lauric	30	—	69·9	264·6	34·4
,,	50	35—36°	46·7	247·5	59·6
Palmitic	20	—	80·1	291·0	18·2
,,	30	51	68·8	286·2	30·5
,,	50	58·5	46·6	281·4	53·9
,,	65	61·5	34·7	276·1	66·1
,,	80	65	18·7	274·0	82·0
Stearic	20	—	74·4	295·2	22·7
,,	50	59	50·1	294·0	48·0
,,	65	63	33·2	296·0	66·5

Each of the esters was oxidised in solution in acetone (at least 10 parts) with powdered potassium permanganate (4 parts), the reaction product being dealt with as described in our previous paper (*loc. cit.*) in order to isolate the fully saturated esters from the acidic products of oxidation; in some cases (where the proportion of combined unsaturated acid was high) it was necessary to repeat the oxidation on the neutral products recovered from the primary oxidation. The results obtained in each case are given in Table IV.

TABLE IV.

Results of oxidation of synthetic glycol di-esters.

Saturated acid.	In synthetic mixed ester, mols. %.	Wt. oxidised, g.	Neutral product, g.	I.V.	Fully saturated glycol esters, % (wt.).	% (mols.).	M. p.
Lauric	34·4	81·6	9·46	0·8	11·6	14·5	44.5°
,,	59·6	48·2 13·2	13·47 12·15	2·9 nil	25·5	29·4	47
Palmitic	18·2	54·95 4·50	4·75 3·50	14·2 nil	6·3	6·9	66
,,	30·5	64·1 11·2	11·47 7·45	13·3 nil	12·0	12·8	67
,,	53·9	66·2	15·70	0·8	23·7	24·8	68
,,	66·1	65·2	25·05	0·9	38·3	39·6	68
,,	82·0	57·0	36·60	nil	64·2	65·3	69
Stearic	22·7	59·0 5·3	5·50 4·60	10·9 nil	8·1	8·1	
,,	48·0	50·0	11·30	0·9	22·6	22·6	73
,,	66·5	55·0	20·00	0·5	36·4	36·4	73

The melting points of glycol dilaurate, dipalmitate, and distearate, observed after recrystallisation from the above specimens, are shown in Table V, together with those of the corresponding fatty acids, their methyl esters, and their triglycerides (Joglekar and

Watson, *J. Ind. Inst. Sci.*, 1930, **13A**, 125). It is noticeable that the glycol di-esters melt in each case at a higher temperature than the triglycerides, which in turn have higher melting points than the free acids.

TABLE V.

Melting points of fatty acids and their methyl, glycol, and glycerol esters.

	Acid.	Methyl ester.	Glycol di-ester.	Tri-glyceride.
Lauric	43·5°	—	49°	46·2°
Palmitic	62·5	28°	69	65·6
Stearic.....................	69·5	39·5	73	71·8

Summary.

1. Glycol esters have been prepared from various mixtures of lauric, palmitic, or stearic acids with oleic acid by heating an excess of each mixture of acids with glycol under reduced pressure.

2. The proportion of fully saturated glycol di-esters in the products has been determined, and it has been found that the content of fully saturated ester varies, with the proportion of saturated fatty acid present in the mixed acids in the esters, in an analogous manner to that observed in similarly prepared synthetic glycerides.

3. In the glycol esters, the molar content of fully saturated ester is not far from, although by no means exactly, proportional to the square of the molar concentration of saturated fatty acids in the mixed acids; in the synthetic glycerides, a similar approximate proportionality to the cube of the latter occurs.

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CXXXI.—*Syntheses of Cyclic Compounds. Part VIII. The Conversion of β-Methyladipic Acid into 3-Methyl*cyclo*pentanone and the Preparation of 3-Methyl*cyclo*pentane-*1 : 1-*diacetic Acid.*

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THE numerous investigations undertaken during the last fifteen years on carbon ring formation and stability have been chiefly concerned with the spatial effect of substituents, more especially in connexion with the Thorpe–Ingold valency deflexion hypothesis :