is improved so as to require little bleaching. The fatty acid-ester content of the distillate is under positive control. Additional unusual design features are:

Two-stage pre-heating of the crude by steam recovered from condensate.
Distilled water for the "boiler-condenser" is assured by use of steam condensate.
Continuous distillation is possible.
Sweetwater is entirely eliminated.
No closed distillate receivers are required.
Separate concentration of distillates is eliminated.

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Computation Forms Relating to the Component Acid Analysis of Marine Animal Oils by the Ester Fractionation Method

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In the ester fractionation procedure (1) for the component acid analysis of natural fats the compositions of the individual fractions are calculated from their determined saponification equivalents and iodine values. With marine animal oils in particular these calculations can be laborious and time-consuming, and we have found the elaboration of definite computation forms of very great assistance; once set up, they enable the compositions of most fractions to be calculated with the assistance of a computor. Moreover the use of such tables provides a concise and permanent record of the computations and great facilitates checking of calculations. In the present communication we therefore record such computation schemes as have been employed in recent component acid analyses of marine animal oils carried out in this laboratory (2). All have been arranged so as to make efficient use of tables of reciprocals, of multiplication tables such as those of Crelle (3), and of computing machines.

Computations relating to fractions containing two saturated plus two unsaturated esters:

The early "solid" and "liquid" ester fractions have been calculated to one or other of the following:

(a) C_{12} and C_{14} saturated plus monoethenoid esters;
(b) C_{14} and C_{16} saturated plus monoethenoid esters;
(c) C_{16} and C_{18} saturated plus monoethenoid esters.

In calculating to these compositions, it has been customary in this laboratory to assume that the S.E. of the saturated portion of each fraction is the same as that of the whole fraction. This assumption leads to little error in the final analysis and does away with the necessity for isolating the saturated ester fraction. The compositions of such fractions may therefore be calculated from equations (1)-(3)

$$x + y + z = w \qquad (1)$$

$$\frac{x}{E} + \frac{y}{E_1} + \frac{z}{E_2} = \frac{w}{E} \qquad (2)$$

$$i_1 y + i_2 z = wi \qquad (3)$$

where w = the weight of the fraction, whose S.E. = E, and I.V. = i.

x = the weight of the saturated C_n plus C_{n+2} esters in the fraction, whose S.E's. E_3 and E_4 are equal to $(E_1 + 2)$ and $(E_2 + 2)$ respectively.

y = the weight of C_n monoethenoid esters of S.E. = E_1 and I.V. = i_1 in the fraction.

z = the weight of C_{n+2} monoethenoid esters of S.E. = E_2 and I.V. = i_2 in the fraction.

The solutions to these equations (1)-(3) are given in equations (4)-(6):

$$z = \frac{wi}{i_1} \cdot \frac{1}{Q + \frac{i_2}{i_1}} = \frac{wi}{i_1} \cdot \frac{1}{Q + \frac{E_1}{E_2}} \qquad (4)$$

since both series of unsaturated esters are monoethenoid and therefore $\frac{i_2}{i_1} = \frac{E_1}{E_2}$

$$y = Q \cdot z \qquad (5)$$

$$x = w - (y + z) \qquad (6)$$

$$\text{where } Q = \frac{E_1}{E_2} \cdot \frac{E_2 - E}{E - E_1}$$

The composition of the saturated ester fraction x may be calculated from the equations (7) and (8):

$$u + v = x \qquad (7)$$

$$\frac{u}{E_3} + \frac{v}{E_4} = \frac{x}{E} \qquad (8)$$

the solutions to which are

$$u = \frac{b - d}{c - d} \cdot x \qquad (9)$$

$$\text{and } v = \frac{c - b}{c - d} \cdot x \qquad (10)$$

where u = the weight of C_n esters of equivalent weight $(E_1 + 2)$ present.

v = the weight of C_{n+2} esters of equivalent weight $(E_2 + 2)$ present.

$$c = \frac{1}{E_3} = \frac{1}{E_1 + 2}$$

$$d = \frac{1}{E_4} = \frac{1}{E_2 + 2}$$

$$b = \frac{1}{E}$$

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TABLE I.

Calculation of the Composition of Fractions Which Are Mixtures of Two Saturated With Two Unsaturated Esters.

1	2	3	4*	5	6	7	8*	9*	10	11*	12*	13*	14	15	16**	17	18*	19*	20
Fraction	w	i	wi	E	E_2-E	$E-E_1$	$E_2-E/E-E_1$	$E_1/E_2[(8)+1]$	wi/i_1	$(8)\cdot E_1/E_2$	$z=(10)/(9)$	$y=(11)\cdot(12)$	$y+z$	$x=(2)-(14)$	$b=10^6/E$	$10^6(b-d)$	$(b-d)/(c-d)$	$u=(15)\cdot(18)$	$v=x-u$
A. Calculation of fractions to C_{12} plus C_{14} saturated and monoethnoid esters: $E_1=212$; $E_2=240$; $i_2/i_1=E_1/E_2=0.8833$; $1/i_1=0.008346$; $c=0.004673$; $d=0.004132$; $1/(c-d)=1848$.																			
L_1	2.29	21.9	49.9	231.2	8.8	19.2	0.458	1.288	0.417	0.405	0.324	0.131	0.455	1.831	4325	193	0.357	0.65	1.18
B. Calculation of fractions to C_{14} plus C_{16} saturated and monoethnoid esters: $E_1=240$; $E_2=268$; $i_2/i_1=E_1/E_2=0.8955$; $1/i_1=0.009452$; $c=0.004132$; $d=0.003704$; $1/(c-d)=2336$.																			
S_1	3.27	3.2	10.5	243.6	24.4	3.6	6.78	6.971	0.099	6.075	0.014	0.085	0.099	3.17	4105	401	0.938	2.97	0.20
C. Calculation of fractions to C_{16} plus C_{18} saturated and monoethnoid esters: $E_1=268$; $E_2=296$; $i_2/i_1=E_1/E_2=0.9053$; $1/i_1=0.01056$; $c=0.003704$; $d=0.003356$; $1/(c-d)=2874$.																			
S_6	6,03	14.3	86.2	272.9	23.1	4.9	4.72	5.17	0.914	4.271	0.177	0.756	0.933	5.10	3664	308	0.884	4.51	0.59

* From multiplication tables or calculating machine.
** From tables of reciprocals.

TABLE IV.

Calculation of "Liquid" Ester Fractions to C_{16} Saturated, C_{16}-2H, and C_{18}-2aH Esters for the Case Where $2a=3.7$,

1	2	3*	4	5**	6	7***	8***	9***	10*	11**	12	13	14	15**	16**
Fraction	E E_1 E_2 E_3	$10^6/E$ $10^6/E_1$ $10^6/E_2$ $10^6/E_3$	$E-E_3$ E_1-E_3 E_2-E_3	$10_5(E-E_3)/E$ $10_5(E_1-E_3)/E_1$ $10_5(E_2-E_3)/E_2$	i i_1 i_2	$10^3i_1(E_2-E_3)/E_2$ $10^3i_2(E_1-E_3)/E_1$ 10^3K****	$10^3i_1(E-E_3)/E$ $10^3i(E_1-E_3)/E_1$ 10^3K_2	$10^3i(E_2-E_3)/E_2$ $10^3i_2(E-E_3)/E$ 10^3K_1	$10_4/K$	w/K	w	y+z	$x=(12)-(13)$	$y=wK_1/K$	$z=wK_2/K$
L_5	281.9 268.0 294.3 270.0	3547 3731 3398 3704	11.9 −2.0 24.3	4221 −746 8257	94.8 94.7 159.6	7819 −1191 9010	3997 −707 4704	7828 6737 1091	1110	0.6638	5.98	3.84	2.14	3.12	0.72

* From tables of reciprocals.
** From multiplication tables or from a calculating machine.
*** K values can be written down directly if calculating machine is used. Entries of components of K are necessary only when multiplication tables are used.
**** Note that K is constant for all calculations as above in which $2a=3.7$.

TABLE V.

Calculation of "Liquid" Ester Fractions to a Mixture of Three Groups of Unsaturated Esters.

1	2	3	4*	5***	6***	7***	8***	9**	10**	11**	12**	13	14	15	16	17
Fraction	i i_1 i_2 i_3	E E_1 E_2 E_3	$10^6/E$ $10^6/E_1$ $10^6/E_2$ $10^6/E_3$	i_2-i_3 i_3-i_1 i_1-i_2	i_2-i_3 i_3-i $i-i_2$	i_3-i_1 $i-i_3$ i_1-i	i_1-i_2 i_2-i $i-i_1$	D_4****	D_1/w	D_2/w	D_3/w	w	w/D_4	x	y	z
L_5	115.2 94.7 107.4 157.7	290.1 268.0 295.5 320.0	3447 3731 3384 3125	−50.3 −63.0 −12.7	−50.3 42.5 7.8	63.0 −42.5 −20.5	−12.7 −7.8 20.5	−0.01416	−0.00519	−0.00547	−0.00351	6.09	−430.1	2.23	2.35	1.51
L_6	123.9 94.7 107.4 157.7	294.4 268.0 295.5 320.0	3397 3731 3384 3125	−50.3 63.0 −12.7	−50.3 33.8 16.5	63.0 −33.8 −29.2	−12.7 −16.5 29.2	−0.01416	−0.00493	−0.00335	−0.00589	5.79	−409.0	2.01	1.37	2.41

* From tables of reciprocals.
** Obtained directly from calculating machine or else individual components of D can be written down in this column from multiplication tables and summed.
*** Note the semi-symmetry of the entries in columns 5, 6, 7, and 8 about a diagonal line.
**** Note that D_4 is constant for adjacent fractions being calculated on the same basis.

TABLE II.

Generalized Computation Form for Calculating the Composition of Any Mixture of Two Saturated With Two Unsaturated Esters.

1	2	3	4	5**	6	7	8	9	10	11	12	13***	14	15**	16**	17**
Fraction	i i_1 i_2	E E_1 E_2	E_2-E $E-E_1$	$E_1(E_2-E)$ $E_2(E-E_1)$	Q* i_2/i_1** $Q+i_2/i_1$	w i/i_1** wi/i_1**	y+z	x= w−(8)	y=Q·z	z= (7)/(6)	E E_3 E_4	$b=10^6/E$ $c=10^6/E_3$ $d=10^6/E_4$	$10^6(b-d)$ $10^6(c-d)$ $10^6(c-b)$	$(b-d)/(c-d)$ $(c-b)/(c-d)$	$u=x(b-d)/(c-d)$	$w=x(c-b)/(c-d)$
S_{16}	94.9 157.7 130.4	343.0 322.0 350.4	7.4 21.0	2383 7358	0.3235 0.8265 1.150	6.97 0.602 4.196	4.83	2.14	1.18	3.65	343.0 326.0 354.0	2916 3068 2825	91 243 152	0.374 0.626	0.80	1.34
S_{18}	111.9 130.4 199.2	360.2 350.4 376.1	15.9 9.8	5568 3685	1.511 1.528 3.039	9.83 0.858 8.434	6.97	2.86	4.19	2.78	360.2 354.0 382.0	2776 2825 2618	158 207 49	0.763 0.237	2.18	0.68

$$* \ Q=\frac{E_1(E_2-E)}{E_2(E-E_1)}$$

** From multiplication tables or calculating machine.

*** From tables of reciprocals.

TABLE III.

Computation Form for Calculating the Compositions of "Liquid" Ester Fractions Which Are Mixtures of Unsaturated Esters Only (Charnley Method).

1	2	3	4	5**	6	7*	8	9	10****	11*	12*	13.	14*	15*	16*	17*
Fraction	•i	E	$10^6 \cdot i/12690$ $10^6(1-F_1/E)$**** $10^6(1+i/12690-F_1/E)$	$10^6/E$	$10^6N_1=(5)-(7)$	$10^6N_2=(4)/28$	$10^6(N_1''-N_1')$	$10^6(N_2'-N_2'')$	$10^9(N_1''N_2'-N_1'N_2'')$	$F_2-2a_2=(8)/(10)$	$F_1-2a_1=(9)/(10)$	w	wN_1	wN_2	$x=(14)\cdot(11)$	$y=(15)\cdot(12)$
A. Evaluation of the composition of "liquid" ester fractions containing C_{18} and C_{20} unsaturated esters only: $F_1=298$; $1/12690=0.00007874$; $1/28=0.03571$.																
L_8	134.0	296.4	10551 −5392 5159	3374	3190	184	−78	−72	−244	319.7	295.1	5.21	0.01660	0.00096	4.90	0.31
L_9	137.8	296.9	10850 −3694 7156	3368	3112	256	−1059	−978	−3315	319.8	295.0	5.01	0.01559	0.00128	4.60	0.41
L_{10}	178.8	304.2	14079 20474 34553	3287	2053	1234	−574	−532	−1801	318.7	295.4	5.16	0.01059	0.00637	3.13	2.03
L_{11}	209.2	308.2	16472 32990 49462	3245	1479	1766	−373	−347	−1172	318.3	296.1	5.63	0.00833	0.00994	2.47	3.16
L_{12}	234.2	310.7	18441 40738 59179	3219	1106	2113	−997	−922	−3126	318.9	295.0	5.69	0.00629	0.01202	1.86	3.83
L_{13}	278.0	318.1	21890 63088 84978	3144	109	3035						6.74	0.00074	0.02045	0.22	6.52
B. Evaluation of the composition of "liquid" ester fractions containing C_{20} and C_{22} unsaturated esters only: $F_1=326$.																
L_{14}	311.0	329.4	24488 10264 34752	3036	1795	1241	467	435	1360	342.6	319.1	6.21	0.01115	0.00770	3.56	2.65
L_{15}	333.3	332.9	26244 20696 46940	3004	1328	1676	598	553	1737	344.3	318.4	5.52	0.00733	0.00925	2.34	3.18
L_{16}	343.6	337.9	27055 35366 62421	2959	730	2229	1***	0***	……..	……..	……..	5.38	0.00393	0.01200	1.25	4.13
L_{17}	347.7	337.8	27378 35040 62418	2960	731	2229	(1064)***	(988)***	(3094)	(343.9)	(319.3)	5.94	0.00434	0.01325	1.38	4.56
C. Evaluation of the composition of "liquid" ester fractions containing C_{22} and C_{24} unsaturated esters only: $F_1=354$.																
L_{16}	155.2	361.0	12220 19420 31640	2770	1640	1130	1020	951	2712	376.1	350.7	2.03	0.00333	0.00229	1.18	0.85
L_{17}	183.1	370.3	14417 43846 58263	2701	620	2081						7.84	0.00486	0.01632	1.70	6.14

* From multiplication tables, or by use of a calculating machine.

** From tables of reciprocals.

*** If accuracy is to be obtained in the evaluation of F_1-2a_1 and F_2-2a_2, then the fractions combined for the purpose must not be too similar in composition. To illustrate this, fraction L_{17}, which cannot be combined with L_{16} to give a significant result, has been combined with L_{14}, and the results are given in brackets.

**** Obtained directly from calculating machine, or else individual components can be written down from multiplication tables and summed.

The computation forms which have been used for calculating the compositions of early "solid" and "liquid" ester fractions, which are mixtures of C_{12} and C_{14} or C_{14} and C_{16} or C_{16} and C_{18} saturated and monoethenoid esters, are illustrated in Tables I(a)-I(e). Because of the frequency with which these three, and in particular the latter two, types of calculation are necessary, it has been found profitable to set up separate forms for each. It will be appreciated, however, that these three are not the only types of calculations of this kind which arise, and we have found that the compositions of individual higher solid ester fractions in particular must sometimes be calculated on the basis that they are mixtures of two saturated and two unsaturated esters. The unsaturated esters have then been assumed to possess the same average unsaturations as determined for them by the application of the Charnley method to the series of "liquid" ester fractions. The necessity for this assumption arises from the imperfection of the lead salt separation in the case of marine animal oils (2). Error must certainly be introduced into such calculations from this and from the earlier assumption that the S.E. of the saturated esters is the same as that of the whole fraction; since very few such fractions occur, the effect on the final analysis is not significant. Table II illustrates the generalised form of computation adopted in this type of calculation.

Computations relating to "liquid" fractions containing C_{18} and higher unsaturated esters only:

The evaluation of the compositions of fractions of the above types has been discussed in detail by Charnley (4). The *composition* of any such fraction is to be obtained from equations (11) and (12), viz.

$$1 + \frac{i}{12{,}690} - \frac{F_1}{E} = 28N_2 \qquad (11)$$

$$\frac{1}{E} = N_1 + N_2 \qquad (12)$$

where i = I.V. of the fraction.

E = S.E. of the fraction.

F_1 = S.E. of saturated esters of the same carbon content (C_n) as the lower molecular weight group of unsaturated esters present in the fraction.

F_2 = S.E. of saturated esters of the same carbon content (C_{n+2}) as the higher molecular weight group of unsaturated esters present in the fraction.

N_1 = mols. of C_n unsaturated esters present in 1 gm. of the fraction.

N_2 = mols. of C_{n+2} unsaturated esters present, in 1 gm. of the fraction.

The *weights of the components* of such fraction are given by

$$x = N_1(F_1 - 2a_1)w \qquad (13)$$
$$y = N_2(F_2 - 2a_2)w \qquad (14)$$

where x = weight of C_n unsaturated esters of average unsaturation $-2a_1H$ present.

y = weight of C_{n+2} unsaturated esters of average unsaturation $-2a_2H$ present.

w = weight of the fraction.

$F_1 - 2a_1$ = S.E. of the C_n unsaturated esters present.

$F_2 - 2a_2$ = S.E. of the C_{n+2} unsaturated esters present.

The number of double bonds, a_1 and a_2, are calculated from the values of N_1 and N_2 obtained in two adjacent fractions, the relevant equations for the calculation being (15) and (16),

$$1 = (F_1 - 2a_1)N_1' + (F_2 - 2a_2)N_2' \qquad (15)$$
$$1 = (F_1 - 2a_1)N_1'' + (F_2 - 2a_2)N_2'' \qquad (16)$$

the solutions to which are

$$F_1 - 2a_1 = \frac{N_2' - N_2''}{N_1'' N_2' - N_1' N_2''} \qquad (17)$$

$$F_2 - 2a_2 = \frac{N_1'' - N_1'}{N_1'' N_2' - N_1' N_2''} \qquad (18)$$

A computation scheme for the evaluation of the compositions of fractions of this type is given in Table III. Data for a number of fractions are given in order to illustrate the variations in the values of (F_1—$2a_1$) and (F_2—$2a_2$) obtainable through the combination of different fractions in the Charnley method.

It is perhaps of interest to note that, from the effect of increasing unsaturation on boiling point (1), it might be expected that in any one series of fractions the degree of average unsaturation in each of the homologous groups of esters would fall as distillation proceeded. In practice (Table III) the results have not exhibited any definite trend but have shown a random scatter. This is probably a reflection of the experimental errors of the I.V. and S.E. determinations of individual fractions.

In practice the mean value for the average unsaturation has been used throughout. Calculation of such average unsaturation from the combination of as many pairs of different fractions as possible minimizes error in the final average and moreover gives an idea of the probable error in the final assessment of the degree of average unsaturation. Such a knowledge is valuable where a comparison of the average unsaturation of a given ester group in different oils is required (5).

Computations relating to fractions containing one saturated and two unsaturated esters:

Fractions of this type may occur in either "liquid" or "solid" series and their compositions are to be calculated from equations (19)-(21),

$$x + y + z = w \qquad (19)$$

$$\frac{x}{E_3} + \frac{y}{E_1} + \frac{z}{E_2} = \frac{w}{E} \qquad (20)$$

$$i_1y + i_1z = wi \qquad (21)$$

in which

w = the weight of the fraction of S.E. = E, and I.V. = i.

x = the weight of saturated ester in the fraction, of S.E. = E_3.

y = the weight of unsaturated ester in the fraction, of S.E. = E_1, and I.V. = i_1.

z = the weight of unsaturated ester in the fraction, of S.E. = E_2, and I.V. = i_2.

The solutions to these equations are

$$y = \frac{wK_1}{K} \qquad (22)$$

$$z = \frac{wK_2}{K} \qquad (23)$$

$$x = w - (y + z) \qquad (24)$$

$$\text{where } K = \frac{i_1(E_2 - E_3)}{E_2} - \frac{i_2(E_1 - E_3)}{E_1}$$

$$K_1 = \frac{i(E_2 - E_3)}{E_2} - \frac{i_2(E - E_3)}{E}$$

$$K_2 = \frac{i_1(E - E_3)}{E} - \frac{i(E_1 - E_3)}{E_1}$$

Computations relating to "liquid" ester fractions containing three unsaturated ester groups only:

Occasionally in the "liquid" ester series of fractions, when, for example, the C_{16} saturated esters have just distilled off, fractions are obtained whose composition can only be calculated on the basis that they contain three groups of unsaturated esters, e.g. C_{16}, C_{18}, and C_{20} unsaturated esters. In such cases the composition of the fraction is to be evaluated from the equations (25), (26), and (27),

$$x + y + z = w \qquad (25)$$

$$\frac{x}{E_1} + \frac{y}{E_2} + \frac{z}{E_3} = \frac{w}{E} \qquad (26)$$

$$i_1x + i_2y + i_3z = wi \qquad (27)$$

where w = the weight of the fraction, of S.E. = E, and I.V. = i.

x = the weight of, say $C_{16} - 2H$ esters present, of S.E. = E_1 and I.V. = i_1.

y = the weight of C_{18} unsaturated esters present, whose S.E. = E_2, and I.V. = i_2.

z = the weight of C_{20} unsaturated esters present, whose S.E. = E_3, and I.V. = i_3.

The solutions to these equations are

$$x = \frac{D_1}{D_4};\ y = \frac{D_2}{D_4};\ z = \frac{D_3}{D_4}.$$

$$\text{where } D_1 = w\left[\frac{i_2 - i_3}{E} + \frac{i_3 - i}{E_2} + \frac{i - i_2}{E_3}\right] \qquad (28)$$

$$D_2 = w\left[\frac{i_1 - i}{E_3} + \frac{i - i_3}{E_1} + \frac{i_3 - i_1}{E}\right] \qquad (29)$$

$$D_3 = w\left[\frac{i_1 - i_2}{E} + \frac{i - i_1}{E_2} + \frac{i_2 - i}{E_1}\right] \qquad (30)$$

$$D_4 = \frac{i_3 - i_1}{E_2} + \frac{i_1 - i_2}{E_3} + \frac{i_2 - i_3}{E_1} = \text{a constant K for each set of fractions.} \qquad (31)$$

In Table V is illustrated the form of computation developed for the calculation of the compositions of fractions of this type.

Computations of the composition of fractions on the basis of saponification equivalents alone:

The compositions of final fractions must often be assessed on the basis of S.E's. only, because oxidation and/or polymerisation reactions occur during distillation with the result that the iodine values of such fractions are often meaningless. In most analyses of marine animal oils the final "liquid" ester fraction has therefore been calculated to a mixture of C_{22} unsaturated esters (of known average S.E.) and C_{24} unsaturated esters, the average unsaturation of which has been taken as C_{24}—10H in the absence of any method of determining the real value.

The equations for the calculations concerned are (7)-(10) and a convenient form of computation is that illustrated in columns 12-17 of Table II.

Summary

Computation schemes have been found of assistance in calculations relating to the component acid analysis of marine animal oils by the ester fractionation method; these are described.

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