

THE GLYCERIDE COMPOSITION OF FATS AND OILS

Part I. Mowrah Oil

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Received May 3, 1944

IN an earlier publication¹ from this laboratory a tentative method for estimating the unsaturated glycerides in fats and oils was suggested. We have commenced the systematic examination of a number of oils in order to get data concerning the glyceride composition, as such data are required in connection with another investigation engaging our attention.

In the original oxidation method developed by Hilditch and co-workers a comparatively large quantity of fat is oxidised. Due to difficulties arising from the war, it became absolutely necessary to economise in chemicals and so we have developed a method, which we feel does not sacrifice accuracy, and in which not more than ten grams of the oil is required to carry out the investigation. The amount of saturated acids present has to be accurately known and in suitable cases we have now utilised a standard method by which this can be accomplished without the usual separation and ester fractionation. The material left after determining the saponification equivalent of the azelao-glycerides is utilised to estimate the percentage of saturated acids according to Bartram's method.²

Mowrah oil has been previously investigated with respect to its component acids by Gill and Shah³; Dhingra, Seth and Speers⁴ and by Hilditch and Ichaporria.⁵ Hilditch and Ichaporria made a detailed investigation of the component glycerides by the fractional crystallisation technique.

EXPERIMENTAL

6.62 grams of the oil was oxidised yielding 3.2412 grams of bicarbonate insoluble fraction containing GS_3 , GS_2A , and GSA_2 . This was saponified with KOH and the alkali used up for saponification corresponded to 33.08 c.c. of 0.5129 N HCl, giving a saponification value of 293.9.

The GS_3 content of the oil was 1% corresponding to an S.V. of 197.7 based on the ratio of the saturated acids.

I. Determination of Saturated Acid Content

9.45 grams of the oil was oxidised, the manganese dioxide eliminated by the bisulphite method, the acidic portions and neutral product taken up in ether, dried, ether removed and the residue hydrolysed. The free acids obtained was subjected to Bertram's separation. In the acetone permanganate oxidation method carried out at the boiling point of acetone, no hydroxy acids are formed, as the intermediate oxidation products are broken up by further oxidation,⁶ a condition which does not always prevail when unsaturated acids are oxidised by alkaline permanganate. Consequently the Bertram separation can be carried out.

3.866 grams of saturated acids (completely free from oxidation products) having an iodine value of 1.7 was obtained. 3.3743 grams of the acids used 24.25 c.c. of 0.5129 N KOH giving an acid value of 206.9; corresponding to a molecular weight of 271.2.

For purposes of calculation C_{16} and lower acids have been taken as palmitic acid and C_{18} and higher acids as stearic acid. The mean molecular weight of 271.2 has to be corrected for an I.V. of 1.7. This iodine value would correspond to $100 \times 1.7/90$ or 1.9% of oleic acid (90 being the I.V. of oleic acid). That is, the mixed acids obtained contain 1.9% of unsaturated acids calculated as oleic acid and 98.1% of saturated acids. The corrected mean molecular weight would be according to the equation

$$271.2 \times 100 = (282 \times 1.9) + ("a" \times 98.1),$$

where "a" is the correct mean molecular weight and 282 that of oleic acid. The correct value (value of "a") is 271.

The next step is to arrive at the proportion of " C_{16} " and " C_{18} " acids in the oil. The difference between the corrected mean molecular weight and the molecular weight of palmitic acid is 15. The difference between the molecular weights of stearic and palmitic acids is 28. Percentage of saturated acids is $(90 - 1.7) \times 3.866/90 \times 9.45$ or 40.15. The percentage content of C_{18} acid is $40.15 \times 15/28$ or 21.5, and of C_{16} acid is 18.65.

II. Calculation of Unsaturated Acid Content

Assuming that only oleic and linoleic acids are present, the unsaturated acid content is calculated as follows:—

The weight of saturated acids in combination as glycerides is $40.15 \times (271.0 \times 3 + 38)/(271 \times 3)$ or 42.0. The iodine value of the oil is 60.4 and the iodine value of the unsaturated glycerides is $(60.4/100 - 42) \times 100$ or 104.1. The iodine value of triolein is 86.2 and of trilinolein is 173.6.

Hence the percentage of trilinolein is $(104.1 - 86.2) \times 58 / (173.6 - 86.2)$ or 11.9. That of triolein there is $58.0 - 11.9$ or 46.1. These figures indicate that approximately one part of linoleic acid to two parts of oleic acid exist in combination giving a mean molecular weight of 281.3. Hence the percentage of unsaturated acids is $(281.3 \times 3 / 281.3 \times 3 + 38) \times 58$ or 55.47. Consequently the percentage of oleic acid will be $282 \times 3 \times 46.1 / (282 \times 3) + 38$ or 44.1. Similarly that of linoleic acid will be 11.4.

It would be profitable at this stage to compare our calculated figures with the experimental results obtained by previous workers^{3,4} and since the figures in the literature are based on total acids whereas our figures are based on oil, our figures have first to be converted into those corresponding to total acids. This can be accomplished by making use of the Hehner value, 95.7, *i.e.*, multiply the percentages obtained on the basis of the oil by the fraction $100/95.7$.

	Weight percentages of acids			
	Ours	Literature ^{3,4,5}		
Stearic acid ..	22.5	(a) 2.0	(b) 27.5	(c) 19.3
Palmitic acid ..	19.5	(a) 27.5	(b) 17.4	(c) 23.7
Oleic acid ..	46.1	(a) 41.0	(b) 44.6	(c) 43.3
Linoleic acid ..	11.9	(a) 13.6	(b) 9.3	(c) 13.7

Two of the workers have reported myristic acid also, and it must be stated that any comparison is subject to the inevitable variations from sample to sample. The above composition by weight corresponds to Stearic 22, Palmitic 20.9, Oleic 45.3 and Linoleic acid 11.8 by molecules.

III. Calculation of Glyceride Composition

The molecular percentages of saturated and unsaturated acids are in the ratio 42.9 to 57.1. The glyceride composition can now be calculated. S.V. for GS_2A is 292.2 and for GSA_2 409.6. These figures are based on the observation that the ratio of the saturated acids is the same in the two types. After correction for 1% of GS_3 present in the oil, the S.V. of the mixture of GS_2A and GSA_2 is:—

6.62 grams of the oil yielded 3.24 grams of the mixture of the two azelao-glycerides and the tri-saturated glyceride. Since this contains the whole of the GS_3 of S.V. 197.7, we arrive at the following ratio, where "b" is the S.V. of the mixture of the azelao-glycerides:

$$293.9 \times 100 = (2 \times 197.7) + (98 \times "b")$$

The value of "b" is 295.9. The weight of GS₂A in the mixture is

$$\frac{3.2412 \times 98 \times (409.6 - 295.9)}{100 \times (409.6 - 292.2)} \text{ or } 3.068.$$

The weight of GS₂U corresponding to this is

$$3.068 \times (271 \times 2) + 282 + 38 / (271 \times 2) + 188 + 38 \text{ or } 3.443.$$

The percentage by weight of GS₂U will be $3.443 \times 100 / 6.62$ or 52.12 which on conversion into mols-percentage will be 52.5.

The molecular percentage of saturated acids has been found to be (*vide supra*) 42.9, that of GS₂U 52.5 and GS₃ 1.0. Hence the percentage of GSU₂ will be $[(42.9 - 1.0) - (52.5 \times 2/3)] \times 3$ or 20.7.

DISCUSSION

It may be of interest to review briefly the work by others on the estimation of the glyceride composition of mowrah oil. Hilditch and Ichaporia (*loc. cit.*) reported GS₃ 1.2, GS₂U 27.8, GSU₂ 71.0 and GU₃ nil. Since these values are evolved from their tri-C₁₈ estimation and component acids, it is not very safe to place absolute reliance on the figures.⁷ An estimate of the maximum and minimum amounts of tri-C₁₈-glycerides can be made from our results. The minimum value is obtained by considering that the GS₂U is composed of palmito-stearo-oleins wherein the maximum of both palmitic and stearic acids are used up. The maximum value is obtained when GS₂U is composed of either dipalmito- or distearo-oleins.

The molecular percentage of stearo-dioleins in GSU₂ is arrived as follows:—The molecular percentage of stearic acid in the oil is 22, and 42.9 is the molecular percentage of saturated acids. Hence 22/42.9 of the total saturated acids in GSU₂ will be stearic acid. Consequently $20.7 \times 22/42.9$ will be stearo-dioleins and $52.5 \times 22/42.9$ will be distearo-oleins (in GS₂U when we consider the maximum value). When we consider the minimum value the figure $52.5 \times 1.1/42.9$ is obtained (1.1 is obtained by subtracting the mol. % of palmitic from that of stearic). The minimum value is 37.8 and the maximum value 63.2. The exact value can be made only by the fractional crystallisation of the azelaoglycerides and this is engaging our attention.

Hilditch and Meara's method⁸ for calculating the glyceride composition has been applied to the case in hand with the following results:—

	GS	GS ₂ U	GSU ₂	GU ₃
Found experimentally (our result) ..	1.0	52.5	20.7	25.8
Based on even distribution ..	0	28.8	71.2	0
C ₁₆ distributed ..	27.8	0	45.3	26.9
C ₁₈ distributed ..	26.9	0	48.0	25.1
Linoleic distributed ..	31.5	17.1	0	51.4
Oleic distributed ..	0	50.3	27.9	21.6
Linoleic between others and then the excess of oleic over linoleo-diolein between stearic and palmitic ..	0	47.0	34.7	18.3

Without entering into the merits of the different methods of distribution it is noteworthy that our experimental values and the values obtained as per the last but one method of distribution show an encouragingly close agreement.

REFERENCES

1. Kartha and Menon .. *Proc. Ind. Acad. Sci.*, 1943, 17, 114.
2. Bertram .. *Z. deutsch Oel und Fat Ind.*, 1925, 45, 733.
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4. Dhingra, Seth and Speers .. *J. S. C. I.*, 1933, 52, 116 T.
5. Hilditch and Ichaporla .. *Ibid.*, 1938, 57, 44 T.
6. ——— and Priestman .. *Analyst*, 1931, 354.
7. ——— and Jones .. *J. S. C. I.*, 1934, 53, 13 T.
- and Maddison .. *Ibid.*, 1940, 59, 162.

(The calculation is also based on the assumption that no distearo-oleins are present and this awaits experimental confirmation.)

8. ——— and Meara .. *Ibid.*, 1942, 61, 117.