



FIG. 1. Study of time under reflux vs. SO₃ content.

Based on the results obtained, the reflux period required for the determination of organically combined SO₃ in sulfated fatty acid esters should be extended at least 2 hr after both layers are clear. In practice, we have found it convenient to carry

• Letter to the Editor

Validity of Gunstone's Acyl Group Distribution Theory in Vegetable Fats Containing Appreciable GS₃

GUNSTONE (1) presented a theory of acyl group distribution of vegetable fats which he stated provides a satisfactory correlation for most of the available data and unifies earlier theories into one covering the whole range of vegetable fats. The validity of this theory was, however, illustrated with only two vegetable fats, *Sapium sebiferum* (2) and *Platonia insignis* (3), that contain more than traces of GS₃. Other data reported in the literature for several vegetable fats is not in full agreement with Gunstone's theory. The data were obtained by rea-

sonably reliable oxidation and crystallization methods and are presented in Table I. The data is for fats wherein full glyceride type structures have been determined along with the proportions required according to Gunstone's and Kartha's theories (4,5) and the Tally Number for each fat with reference to each theory.

The Tally Number (TN) is a method for obtaining a reasonable numerical idea of the agreement between experiment and theory in glyceride type structure studies in keeping with present day stan-

TABLE I
Analysis of Sulfated Materials for Combined SO₃ at Various Reflux Periods

Time under reflux (Hr)	Combined SO ₃ (%) ^a			
	2	6	16	24
Material sulfated				
n-Propyl tallate	7.32	7.86	7.92	7.92 (4) ^b
Iso-octyl tallate	5.98	6.30	6.34	6.34 (6) ^b
Propyl oleate	7.60	8.06	8.16	8.14 (4) ^b
Tall oil fatty acid	7.12	7.12	7.12	7.12 (1) ^b
Ricinoleic acid	4.34	4.42	4.50	4.50 (3) ^b
Castor oil	5.70	5.78	5.78	(2) ^b

^a Per cent SO₃ was determined on material as is.

^b Time (hr) required for both layers to be clear.

out the hydrolysis by heating the mixture under reflux overnight (ca. 16 hr) and titrating the samples the following day. Using this method, duplicate runs, by one operator, normally do not vary by more than 0.02% SO₃.

J. T. GEOGHEGAN

C. O. MYATT

M. RODSON

Arizona Chemical Company
Stamford, Connecticut

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TABLE I
Glyceride Type Structures of Some Vegetable Fats Containing Appreciable GS₃

Fat	1(c) ^a	2(c)	3(o) ^b	4(c)	5(o)	6(o)	7(o)	8(o)	9(o)
Sm	73	65	54	53	51	82	74	77.5	92.6
Glyceride type structure, experimental, moles %									
GS ₃	21	20	9	8	9	57	42	47	81
GS ₂ U	77	55	54	54	48	33	40	40	17
GSU ₂	2	26	28	32	31	8	15	13	2
GU ₃	0	0	9	6	12	2	3	0	0
Glyceride type structure, calculated, Gunstone's theory, moles %									
GS ₃	19	0	0	0	0	46	22	33	78
GS ₂ U	81	96	65	63	58	54	78	67	22
GSU ₂	0	5	31	33	37	0	0	0	0
GU ₃	0	0	4	4	5	0	0	0	0
Tally number	8	81	28	20	32	42	78	54	10
Glyceride type structure, calculated, Kartha's theory, moles %									
GS ₃	19	20	9	8	9	55	40	46	80
GS ₂ U	81	58	53	51	45	36	43	41	19
GSU ₂	0	19	30	33	35	8	15	12	1
GU ₃	0	3	8	8	11	1	2	1	0
Tally number	8	13	4	6	8	6	6	4	4

^a c-GS₃, GS₂U by crystallization.

^b o-GS₂U by azelaoglyceride estimation; GS₃ by crystallization where S is above C₁₈ and by acetic acid-acetone-permanganate oxidation where S is below C₁₈.

- Key: 1. *Sapium sebiferum* (Meara and Gupta, *J. Chem. Soc.* p 1337, 1950).
 2. *Platonia insignis* (Hilditch and Pathak, *J. Chem. Soc. Suppl.* #1, p 587, 1949).
 3. Palm oil (Kartha, *JAOS* 30, 326, 1953; 31, 85, 1954).
 4. Palm oil (Hilditch and Maddison, *J. Soc. Chem. Ind.* 59, 67, 1940).
 5. Palm oil (Luddy, et al., *JAOS* 31, 266, 1954).
 6. *Myristica malabarica* I (Kartha, *J. Sci. Ind. Res.* 13A, 72, 1954).
 7. *Myristica malabarica* II (Kartha and Narayanan, quoted in Kartha, *J. Sci. Ind. Res.* 21A, 577, 1962).
 8. *Myristica attenuata* (Kartha and Narayanan, *J. Sci. Ind. Res.* 21B, 494, 1962).
 9. *Myristica fragrans* (Kartha and Narayanan, *J. Sci. Ind. Res.* 21B, 442, 1962).

dards of experimental accuracy by the most reliable, though not necessarily the most modern, methods. TN is obtained by summing the numerical differences (irrespective of sign) between the experimental and calculated values for each of the four different glyceride types. The GS_2U can now be determined correctly to $\pm 0.75\%$ by gravimetric chemical methods and hence, according to present day standards, TN of 0-6 means good agreement, 7-12 fair agreement, and 13-20 means serious cause for disagreement, possibly due to the presence of some interfering non-fatty impurity. TN above 20 usually means irreconcilable disagreement between experiments and theory and may perhaps mean non-relevance of theory concerned in the context considered. With Sm (saturated acids, moles %) above 90% GS_3 contents according to random distribution and Gunstone's theory are too close together; hence, agreement at Sm above 90 has little significance. In the fats in Table I, TN for Gunstone's theory is 20 and above for 7 out of the 9 fats showing no resemblance of an agreement and it is in fair agreement only for a single fat with Sm below 90. The second theory considered shows good or nearly good agreement in all cases except one where the results quoted have been obtained by crystallization.

Adequate reliable data is already present in the literature to show that even among natural vegetable fats GS_3 contents and glyceride type structures are not just dependent on saturated acid content alone as claimed by Gunstone's theory. Kartha's theory leaves the GS_3 to a biologic source factor over all ranges of saturated acid composition subject to a maximum value as required by random distribution and merely outlines the changes in glyceride type structures produced when GS_3 differs from random distribution values for individual fats. It is clear (Table I) that it gives a good prediction of glyceride type structures from S and GS_3 contents in vegetable fats containing appreciable GS_3 .

A. R. S. KARTHA
Division of Chemistry
Indian Agricultural Research
Institute
New Delhi, India

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