THE IODINE NUMBER AND THE UNSATURATION NUMBER OF FATS

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In determining the degree of unsaturation and the acid composition of fats, the thiocyanogenometric method is generally used. To determine the acid composition of fats by this method it is necessary to know two indices: the iodine number (I. No.) and the thiocyanogen number (T. No.). In spite of the multiplicity of the variants of the determination of iodine numbers proposed at various times, we cannot be certain of the reliability of the indices obtained, as has been observed by several authors [1-4]. The same remarks relate to the thiocyanogen number. The calculation of the fatty acid composition from the I. No. and T. No. is always based on the assumption that the fat contains unsaturated acids of the C_{18} series. In actual fact, in addition to acids of the C_{18} series, some vegetable and animal fats contain acids with hydrocarbon radicals of different lengths [5]. The figures of Table 1 show how strongly the theoretical iodine numbers of the fatty acids frequently encountered in natural fats differ from the iodine numbers of oleic, linoleic, and linolenic acids. It can be seen from Table 1 that the iodine numbers of the monoenic acids range from 69 to 112 and those of the dienic acids from 150 to 200, depending on their molecular weights. Consequently, the use of "averaged" iodine numbers leads to incorrect results.

Furthermore, the degree of halogenation of the unsaturated acids depends on the position of the double bond with respect to the carboxyl and on the mutual positions of the double bonds in the polyenic acids, i.e., whether they are isolated or conjugated, and, finally, on the configuration of the molecule at the position of the double bond (cis-trans), and therefore it is clear that the I. No. can be considered only as a rough indication of the degree of unsaturation of fats and is unsuitable for determining the fatty-acid composition of glycerides and also the kinetics and chemistry of fat hydrogenation processes.

The latter process is accompanied by phenomena of cis-trans isomerization and by the migration of double bonds (both in the direction of the carboxyl and in the direction of the methyl group) which is accompanied to a considerable extent by the formation of conjugated systems. All this does not necessarily affect the I. No.

Attempts to replace the I. No. for characterizing the degree of unsaturation of fats by "hydrogen" and "hydrogenation" numbers have led to the conclusion that these indices have the same defects as the I. No. [6].

Various forms of chromatography for determining the acid composition of fats give considerably more reliable results than the thiocyanogenometric method. Knowing the acid composition, it is easily possible to calculate the true I. No. of triglycerides from the figures in column 6 of Table 1.

Table 2 gives the experimental and true iodine numbers of several samples of fats that we have studied.

It can be seen from Table 2 that, while for cottonseed oil the calculated iodine numbers agree more or less with those found experimentally, for the oil of the celery cabbage (family Cruciferae) and ligusticum (family Umbelliferae) the experimental iodine numbers do not correspond to the composition of these oils at all. This applies in even greater measure to the hydrogenizates.

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TABLE 1. Theoretical Iodine Numbers of Fatty Acids and Their Glycerides

Acid	Formula	Number of double bonds, m	I. No. of the fatty acid, % I_2	I. no. / m	I. No. of glycerides, % I_2	I. No. of f.a. / I. No. of glycerides
Myristoleic	$C_{14}H_{26}O_2$	1	112,1	112,1	106,2	1,056
Palmitoleic	$C_{16}H_{30}O_2$	1	99,8	99,8	95,0	1,051
Oleic	$C_{18}H_{34}O_2$	1	89,9	89,9	86,0	1,045
Eicosenoic	$C_{20}H_{38}O_2$	1	81,8	81,8	78,5	1,042
Erucic	$C_{22}H_{42}O_2$	1	75,0	75,0	72,3	1,038
Tetracosenoic	$C_{24}H_{46}O_2$	1	69,2	69,2	66,9	1,034
Hexadecadienoic	$C_{16}H_{28}O_2$	2	201,2	100,6	191,8	1,049
Linoleic	$C_{18}H_{32}O_2$	2	181,1	90,5	173,2	1,045
Eicosadienoic	$C_{20}H_{36}O_2$	2	164,5	82,2	158,1	1,041
Docosadienoic	$C_{22}H_{40}O_2$	2	150,8	75,4	145,3	1,038
Hexadecatrienoic	$C_{16}H_{26}O_2$	3	304,2	101,4	289,5	1,051
Linolenic	$C_{18}H_{30}O_2$	3	273,7	91,2	261,6	1,046
Eicosatrienoic	$C_{20}H_{34}O_2$	3	248,4	82,8	238,5	1,041
Octadecatetraenoic	$C_{18}H_{28}O_2$	4	367,3	91,8	351,2	1,046
Arachidonic	$C_{20}H_{32}O_2$	4	333,5	83,4	320,2	1,042
Eicosapentaenoic	$C_{20}H_{30}O_2$	5	419,6	83,9	402,8	1,042
Docosapentaenoic	$C_{22}H_{34}O_2$	5	384,1	76,8	369,9	1,038
Clupanodonic	$C_{22}H_{32}O_2$	6	463,8	77,3	446,4	1,039

TABLE 2. Experimental and True Iodine Numbers of Fats of Different Compositions

Acid	Cottonseed oil	Celery cabbage [7]	Lemay's ligusticum	Samples of hydrogenates № 1	№ 2	№ 3
Tridecanoic	—	0,34	—	—	—	—
Myristic	—	—	0,90	0,78	0,01	1,10
Pentadecanoic	—	1,37	—	—	—	—
Palmitic	22,08	5,66	4,60	21,66	21,94	23,86
Stearic	2,60	2,32	1,01	2,44	4,21	13,27
Palmitoleic	—	1,57	1,29	1,85	2,14	1,96
Oleic	23,10	17,08	33,52	19,08	23,43	46,89
Petroselinic	—	—	22,88	—	—	—
Linoleic	52,22	17,23	30,40	54,19	47,27	12,92
Linolenic	—	22,10	5,40	—	—	—
Eicosenoic	—	9,13	—	—	—	—
Eicosadienoic	—	3,64	—	—	—	—
Erucic	—	19,60	—	—	—	—
Calculate iodine number, % I_2	110,31	130,89	116,50	112,02	104,05	64,56
Experimental iodine number, % I_2	108,60	115,59	107,60	104,37	88,20	59,90
Experimental error, % rel.	−1,55	−11,69	−7,12	−6,83	−15,28	−7,22
Unsaturation number	127,54	155,38	134,69	129,31	120,11	74,69

Consequently, we consider it desirable in investigations on the kinetics of the hydrogenation process to use in place of the I. No. a different index – the "unsaturation number" (U. No.), showing the total number of double bonds in 100 molecules of fatty acids and calculated from the formula

$$1 \cdot \sum N' + 2 \cdot \sum N'' + 3 \cdot \sum N''' + \cdots,$$

where $\Sigma N'$ is the number of molecules of monoenic acids in 100 molecules of total acids present in the mixture;

$\Sigma N''$ is the number of dienic molecules;

$\Sigma N'''$ is the number of trienic molecules, and so on; and 1, 2, 3, . . . are the numbers of double bonds in the acid molecules.

This is provided that the fatty-acid composition is determined by one of the methods not giving rise to uncertainty. The values of the U. No. calculated by this method are given in the last line of Table 2.

TABLE 3

Acid	No. of double bonds	Mol. wt. of acid	Wt. %	Rel. no. of mole-cules, n	Molar %, N
A_1	0	M_1	a	a/M_1	$k^*.a/M_1$
A_2	0	M_2	b	b/M_2	$k.b/M_2$
A_3	0	M_3	c	c/M_3	$k.c/M_3$
A_4	1	M_4	d	d/M_4	$k.d/M_4$
A_5	1	M_5	e	e/M_5	$k.e/M_5$
A_6	1	M_6	f	f/M_6	$k.f/M_6$
A_7	2	M_7	g	g/M_7	$k.g/M_7$
A_8	2	M_8	h	h/M_8	$k.h/M_8$
A_9	3	M_9	i	i/M_9	$k.i/M_9$

*Recalculation factor $k = 100/\Sigma n$.

TABLE 4

Index	Iodine No.	Samples of hydrogenizates taken			Mean value of $K^* \cdot 10^2$
		5	10	19,2	
Content of acids,%					
Myristic	1,12	0,87	0,85	0,92	—
Palmitic	22,13	22,47	23,23	22,51	—
Palmitoleic	1,50	1,33	1,25	1,90	—
Stearic	1,33	1,48	2,39	3,06	—
Oleic	17,41	25,89	51,20	59,95	—
Linoleic	56,51	47,96	21,08	11,66	—
Experimental I. no.	110,80	88,00	81,49	69,49	3,20
Calculated I. No.	114,27	105,33	81,73	73,54	2,39
U. No.	131,93	123,14	94,61	85,17	2,64

*Rate constant of the reaction.

It follows from what has been said that the U. No. is calculated from the composition of the fatty acid mixture expressed in molar percentages, in contrast to the I. No. which is calculated from the composition of the mixture expressed in percentages by weight. The iodine number of each acid depends on the number of double bonds in its molecule and on its molecular weight; the U. No. depends only on the number of double bonds.

If a method the results of which are expressed in molar percentages (for example, the densitometric or radioactivation method for the quantitative evaluation of paper chromatograms) is used to determine the composition of a mixture of fatty acids, the figures obtained in this way form the basis of the calculation by the formula given above. If the method gives the results of the determination of the composition in percentages by weight (for example, determination by gas-liquid chromatography), these results are recalculated to molar percentages (Table 3). This table gives the composition of a mixture of three saturated, three monoenic, two dienic, and one trienic acids.

One of the advantages of the U. No. is its generality for acids and glycerides. Although one molecule of a monoacid glyceride is equivalent in respect to the number of fatty acid radicals present in it to three molecules of fatty acids, the number of double bonds in such a glyceride molecule is three times larger than in a molecule of fatty acid.

Thus, the U. No. of any unsaturated fatty acid coincides with the U. No. of the corresponding monoacid triglyceride. Consequently, on passing from fatty acids to glycerides or conversely no recalculation of the U. No. is necessary as it is in the case of iodine numbers. By using the information from this table. we can determine the U. No. from the formula

$$\left[\left(\frac{d}{M_4}+\frac{e}{M_5}+\frac{f}{M_6}\right)\cdot 1+\left(\frac{g}{M_7}+\frac{h}{M_8}\right)\cdot 2+\frac{i}{M_9}\cdot 3\right]\cdot\frac{100}{\sum n}.$$

Table 4 gives the results of one of the series of experiments which we have described previously [9] on the hydrogenation of cottonseed oil. It can be seen from the table that the rate constant of the reaction calculated from the U. Nos. is extremely close to that obtained from the calculated I. Nos.

In proposing to introduce the new index U. No. into the practice of investigations on fats we are giving not yet another variant of the I. No., but a completely new magnitude.

Between correctly determined iodine and hydrogen numbers a strict proportionality must exist, and if the hydrogen numbers are recalculated to iodine, the two indices should coincide. There can be no agreement or proportionality between U. Nos. and iodine Nos. since all the monoenic acids enter the calculation formula for the U. No. with the same factor 1, all the dienic acids with the factor 2, and so on, regardless of the molecular weight of the acid, while the values of the iodine numbers differ according to the molecular weights.

SUMMARY

In order to determine the degree of unsaturation of fats and to study the kinetics of their hydrogenation, it is proposed to use instead of the iodine number an index which is called the unsaturation number and shows the total number of double bonds in 100 molecules of fatty acids.

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