A Study of the Bolton and Williams Grouping of Fatty Oils According to the Iodine Number of Their Unsaponifiable Matter

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For distinguishing between pure olive oil and olive oil adulterated with other oils, E. R. Bolton and K. A. Williams (Analyst, 55, 5 (1930)) have suggested the use of the iodine numbers of the unsaponifiable matter. Upon this basis, these authors divided the fats and oils into the following four groups: Group 1—iodine numbers 64 to 70—contains the land animal fats and the coconut group of oils. Group 2—iodine numbers 90 to 96—contains the oils from fish, marine animals, and cacao butter. Group 3—iodine numbers 117 to 124—contains the majority of vegetable fats and oils. (The unsaponifiable matter of crude soy-bean oil gives iodine numbers between 75 and 120, that from the refined oil gives values from 117 to 124.) Group 4—iodine numbers 197 to 206—contains only olive oil. The iodine numbers were determined by the Rosenmund and Kuhnhenn method (Z. Nahr. Genussm. 46. 154 (1923)). As this procedure appeared promising for the detection of tea seed oil, as well as for other oils which are at times used to adulterate olive oil, the Olive Oil Committee of the American Oil Chemists' Society undertook a collaborative study of the method in order to ascertain whether the method would definitely detect tea seed oil in an olive oil to which 20 per cent of tea seed oil had been added. As a part of the committee working on this study we obtained the following results:

TABLE I

Oil	Unsaponifiable Matter Per Cent	Iodine Number of Unsaponifiable Matter
Olive, No. 1	0.86	213
	0.88	162
Olive, No. 2	0.92	255
	0.93	244
Olive, No. 3—20% Tea Seed	0.96	248
	1.01	190
	1.06	196
	0.94	255
	0.85	262

Similar discouraging results were obtained by other collaborators, although every detail of the method was carefully followed. We suspected that the trouble was chiefly due to the method given, which directs but three extractions with petroleum ether. In many cases seven extractions are required with petroleum ether, and sometimes even more, in order to get all the unsaponifiable matter. A difference of but a few hundredths of a per cent makes a large variation in the iodine numbers, particularly in the case of the unsaponifiable matter from olive oil. From the present investigation, it is evident that the olive oil unsaponifiable matter is composed of a number of substances widely different in composition. It appears that the more saturated constituents are extracted with more difficulty than the others because the smaller the quantity of the unsaponifiable matter obtained, the higher is its iodine number.

A second objection to the method is that washing the petroleum ether extract with one portion of dilute alkali solution is seldom sufficient to remove all the dissolved soap, some of which is liable to remain in the form of acid soaps with the unsaponifiable matter.

We decided to continue the study of the Bolton and Williams method but to substitute the well-known modified Kerr-Sorber procedure (J. Assoc. Off. Agric. Chem. 8, 439 (1925)) for the extraction of the unsaponifiable matter. In this procedure the saponified oil is dissolved in ether, then the soap is extracted from this solvent, in which remain the unsaponifiable constituents. There are a few points to be discussed concerning the use of this method, when the iodine number of the unsaponifiable matter is to be determined. As the highly unsaturated unsaponifiable substances from olive oil are readily susceptible to oxidation, it is necessary to remove the last of the ether and moisture from the unsaponifiable residue in an oven with an atmosphere of carbon dioxide or nitrogen. If it is not possible to determine the iodine number within a few hours the unsaponifiable matter should be kept dissolved in ether in a dark, cool place. A properly adjusted balance should be used with weights standardized by the Richards method (J. Amer. Chem. Soc. 22, 144 (1900)). Also counter-balanced flasks should be used in weighing the unsaponifiable matter, to take care of changes in humidity and room temperature. Flasks should not be wiped with a dry towel, as this will frequently produce an electrostatic charge on the flask that is difficult to remove. It has been found satisfactory to wipe the flasks, at times, with a clean towel made damp with alcohol. After drying and cooling, the flasks are ready for weighing. Attention is also called to the importance of maintaining the volume of ether close to 150 cc. during the analysis, otherwise small quantities of the unsaponifiable matter are liable to be lost. Also, the ether solution must be washed with the recommended dilute alkali solution until the soap is completely removed. The presence of soap in the alkali wash waters is detected by strongly acidifying them with hydrochloric acid, and after thorough mixing, allowing the solution to stand for several minutes. The appearance of more than a trace of turbidity indicates that further washing of the ether with the alkali solution is necessary before the final washing with water.

The following results were obtained with the samples submitted for the collaborative study. The modified Kerr-Sorber method was used for extracting the un-

saponifiable matter, and its iodine number was determined by the Rosenmund-Kuhnhenn procedure:

TABLE II

Oil	Unsaponifiable Matter Per Cent	Iodine Number of Unsaponifiable Matter
Olive, No. 1	1.14	205
	1.10	208
	1.10	207
	1.08	209
Olive, No. 2	1.14	213
	1.14	211
Olive, No. 3—20% Tea Seed	1.27	204
	1.28	206
	1.27	202

It will be observed that the quantities of unsaponifiable matter obtained in each case are distinctly larger than those given in Table I and the range of the iodine numbers for each sample is small, which clearly indicates the uniformity of the composition of the unsaponifiable matter.

Then the method was applied to three different samples of tea seed oil with the following results:

TABLE III

Oil	Unsaponifiable Matter Per Cent	Iodine Number of Unsaponifiable Matter
Tea Seed No. 1	0.75	164
Tea Seed No. 2	0.92	154
Tea Seed No. 3	0.74	151

Sample No. 1 was the oil used in the collaborative tests (loc. cit.). Evidently, tea seed oil could not be included in Bolton and Williams Group 3, in which the iodine numbers range from 117 to 124.

In the same manner several other oils were examined, and the following results were obtained:

TABLE IV

Oil	Unsaponifiable Matter Per Cent	Iodine Number of Unsaponifiable Matter
Refined Cottonseed	0.56	107
Rape Seed	0.89	108
Peanut	0.47	113
Italian Olive	0.94	254
	0.94	252
	0.91	261

In order to get further data on the variation in the iodine number of the unsaponifiable matter of olive oil, it was necessary to obtain authentic samples from widely different localities. Through the kindness of Mr. Nathan Herrwitz, European representative of the Van Camp Packing Company, we obtained the desired samples. These have recently been examined, with the following results shown in table V.

Bolton and Williams state that the range for the iodine numbers of the unsaponifiable matter of olive oil is from 197 to 206, but from the results given above it should extend from 190 to 268 for oil of the first pressing. The low iodine number for the unsaponifiable matter from refined pulp oil is noteworthy and suggests the possibility of using the method for the detection of refined olive oil in admixture with olive oil of the first pressing, providing that the olive oil is known not to be from Tunis. The iodine numbers in Table V, other than those of the unsaponifiable matter from Tunisian olive oils, range from 212 to 268.

TABLE V

Olive Oil	Unsaponifiable Matter Per Cent	Iodine Number of Unsaponifiable Matter
California	1.09	208
Italian—Bitonto	0.82	240
Italian—Bitonto No. 2	0.94	255
Italian—Bitonto—Calabra	0.76	232
Spanish—Boyas	0.68	227
Spanish—Boyas	0.64	229
Spanish—Natural Leridas	1.05	241
Spanish—Andalusian	1.02	268
Grecian—Metelin	0.78	213
French—Provence	1.01	242
Algerian—Extra natural	0.66	245
Tunisian—Sousse	0.71	195
Tunisian—Sousse	0.69	197
Tunisian—Sfax	0.69	190
Tunisian—Sfax (2nd pressing)	0.73	180
Refined pulp oil	1.68	119

G. Loew (Olii e Grassi 11, 10 (1931)) examined a number of second and third pressing oils, and a refined olive oil. The iodine numbers of the unsaponifiable matter, in these cases, ranged from 125 to 168. For corn, grape, peanut, rape, sesame, and sunflower oils, he found the range to be from 96 to 130. It will be observed that the one sample of second pressing oil (Table V) gave a much higher result, whereas the refined pulp oil gave a notably lower result than those obtained by Loew.

From our results alone it is evident that the grouping of the oils which we have investigated requires considerable revision in regard to the range of the iodine numbers of their unsaponifiable matter.

Summary.—A critical study has been made of the methods used by Bolton and Williams for the separation of the unsaponifiable matter from fatty oils, and the determination of its iodine number. Owing to the very erratic results obtained, a further study was made in which the only change was the use of the modified Kerr-Sorber procedure for obtaining the unsaponifiable matter in place of the one suggested. With this procedure reasonably consistent results were obtained, but they were not in agreement with those reported by Bolton and Williams. The present investigation, in the case of olive oil of the first pressing from widely different sources, has shown that the range of the iodine numbers of the unsaponifiable matter is very much wider than that found by Bolton and Williams, whereas the iodine numbers found for refined cottonseed, peanut and rape oils were distinctly below their Group 3 range (117-124) and that for tea seed oil (151-164) was much above it.

Although the values for refined pulp or pomace oil, second and third pressing olive oils, and those of the common seed oils are very much below those of olive oil of the first pressing, the extreme range of the latter prevents the use of the method for regulatory purposes