

determinations and is always ready for use.

Experimental data

In comparing the two methods, we at first used samples of commercially dehydrated castor oil containing an unknown amount of $\Delta^9,11$ -linolic acid. The Kaufmann method was employed with the single variation that the maleic acid was titrated with N/6 alcoholic KOH instead of with N/10 aqueous NaOH. The oven temperature could not be controlled any better than about $\pm 5^\circ$ C. In carrying out the Ellis method we followed the instructions given for the short time variation (in presence of iodine) since equal accuracy is claimed for both variations. However, instead of using a spiral condenser we were satisfied with a straight air condenser with ground connection to the flask after ascertaining by a number of blank runs that no appreciable amounts of maleic anhydride were lost in this procedure (Table 1). The toluene as well as the acetone used was Baker's c. p.; the maleic anhydride was the same in both cases.

TABLE 1—Blank Runs with Different Periods of Refluxing (Ellis Method)

Date	Apr. 5, '37	Apr. 6, '37	
ml KOH consumed..	28.53	28.50	No refluxing, hydrolized in separatory funnel.
	28.53	28.40	Refluxed directly with H ₂ O 15 minutes.
	28.30		Refluxed 1 hour before adding water.

In order to compare not only the methods directly but at the same time the dependence of the results upon minor factors, such as the weight of the samples, the latter were allowed to vary about 100% in the duplicates; also the period of heating was varied about 100% in

one of the determinations by the Kaufmann method. The following table shows the results:

It will be noted that the values obtained by the two methods disagree considerably (up to 50%), the Ellis method giving the higher results. Furthermore, in both cases the results depend on the weights of sample used, though this variation is considerably greater in the Ellis method.

A sample was then tested which could not possibly contain any conjugated double bonds. We suspected that the higher values obtained with the Ellis methods might be caused by the presence of hydroxy acids or their esters in some of the investigated samples (the value of 10.5 for medicinal castor oil for instance which E. and J. found seems unusually high). We therefore used hydrogenated castor oil with an iodine number of 1.2 for this test.

The maleic value obtained by the

lar to an acetylation. We have not identified the reaction product formed, but we were able to show that the maleic anhydride has actually reacted with the oil and has not just been lost through experimental conditions: We thoroughly washed the product obtained in a parallel run, (similar in all details to the Ellis procedure) with hot water until the last traces of maleic acid were removed as shown by neutrality to methyl-orange. The saponification number of the product then was 192.5 as compared with 180.6 for the untreated hydrogenated castor oil. This increase of 11.9 in the sap. number corresponds to a maleic value of about 3.4; a fairly good agreement with the results shown in Table 3.

Conclusions

Our analytical data show that with certain compounds the Ellis method gives too high results. They also show that the results obtained by the Ellis method depend

TABLE 3—Comparison on Hydrogenated Castor Oil, Iodine Number = 1.2

Ellis Method		Kaufmann Method	
Wght. of Samples	Maleic Value	Wght. of Samples	Diene Value
6.299	4.2	1.904	0.23
10.225	3.9		

Ellis method in this case obviously cannot represent any double bonds. Apparently, some maleic anhydride reacts in a different way than the Diene-synthesis of Diels and Alder³). Probably a reaction with hydroxyl groups takes place simi-

³Annalen 460, 98 (1928).

to a greater extent upon the weight of sample used than those found by the Kaufmann method. No indications have been observed in these experiments as well as in other routine determinations to support the statement that the Kaufmann method is unreliable.⁴ However, a need is felt for a method which would combine the greater reliability of the Kaufmann method with the greater speed of the Ellis method.

No reason can be seen for renaming the original method after a few changes. Priority rights are due to H. P. Kaufmann and his co-workers. His "Diene Value" indicates exactly the quantitative evaluation of conjugated double bonds.

⁴Berichted d.D. Chem. Ges. 70, 900, 903, 908 (1937).

TABLE 2—Comparison of Both Methods with Duplicates of Varying Weights of Sample

Material	Ellis Method		Diff.	Kaufmann Method		Discrepancy between the methods
	Wght. of Sample	Maleic Values		Wght. of Sample	Diene Values	
Dehydrated Castor Oil...	3.001	20.8	} 2.6	0.3167	14.1	} 1.1
Dehydrated Castor Oil... Average	5.999	18.2		0.5892	13.0	
Distilled Fatty Acids from Dehydrated and Split Castor Oil	3.019	26.8	} 5.5	0.2553	16.8*	} 1.4
Average	6.020	21.3		0.5158	15.4**	
		24.1			16.1	8.0

*In oven at 95-100° C. for 40 hrs.

**In oven at 95-100° C. for 21 hrs.

REPORT OF REFEREE BOARD

The activities of the Referee Board for the past year included the usual appointment of Referee Chemists and distribution of 10 cottonseed samples and 5 crude cottonseed oil samples for collaborative test by the Referee Chemists and voluntary collaborators.

Thirty-three Referee Certificates were issued. The names of the Referee Chemists were published in OIL AND SOAP and need not be

reproduced in the present report.

The average standard of work of our Referee Chemists is believed to be even higher than formerly. Most of the credit for this must be given to the efforts of the Referee Chemists themselves, but there are definite indications that the activities of the Referee Board in connection with the collaborative samples, including the check meal samples of the Smalley Foundation Committee,

have had a beneficial effect. The committee's only recommendation is that the collaborative test samples be continued, and all the collaborators are invited to offer constructive criticism for improvement of the program. J. P. HARRIS

N. C. HAMNER
E. C. AINSLIE
J. J. VOLLERTSEN
A. S. RICHARDSON
Chairman.