

this, but it seemed best to replace the 110 volt current in the control circuit, and in accordance with the suggestion at the end of my note (*supra*) a Westinghouse bell-ringing transformer was connected with its primary across the main supply, and the relay and thermoregulator operating on the outside 24 v. secondary terminals. This arrangement has given practically no trouble, and is at present used on the large incubator described; on three gas-heated water baths, using the Beans electromagnetic gas valve; and on a large electrically heated air-current drier, taking about 30 amperes in the heating circuit; in the latter case, the 200 ohm relay operating on the 24 v. circuit controls a branch of the 110 v. circuit which operates a large motor-starting relay ("Contactor"), the coil of which takes 0.4 ampere. Two different makes of these contactors are at present in satisfactory use in this Institute, one A. C., and the other D. C. They are rather clumsy for handling currents of less than 15 amperes, and there would appear to be some demand in laboratories for a well-constructed relay operating on 110 v. A. C. or D. C., to control circuits carrying from 2 to 15 amperes—such relays do not appear to be made at present; the ordinary main line relay will usually take care of 2 amperes, though the lead to the armature may warm up a little.

I believe that the lower voltage at the break is a decided advantage; the little bell-ringing transformers take very little current, and one will operate a large number of such temperature-control circuits.

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THE DETERMINATION OF VOLATILE ESTERS IN CITRUS OILS AND EXTRACTS.

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I. Theoretical.—The citrus oils have been shown, by a large number of investigators, to be very complex mixtures, as is true of practically all of the volatile oils. The principal representatives of the class, lemon and orange oils, are very similar in composition.¹ Each contains over 90% of hydrocarbons, the terpene *d*-limonene being in preponderance. Aldehydes constitute about 4–6% of lemon oil, about 1–3% of orange oil. Citral is the most important member of this group present, but is accompanied by smaller proportions of citronellal and other aliphatic members such as nonyl and decyl aldehydes. A number of other substances are present, to which some of the finer characteristics of the odors of the oils are due. The most important of these are the esters, the identity of which has been fixed as linalyl and geranyl acetates.²

¹ "The Volatile Oils," by Gildemeister & Hoffman.

² Umney and Swinton, *Pharm. J.*, 61, 196, 370 (1898).

Fairly satisfactory methods have been elaborated for the examination of the oils, in so far as regards the physical properties and the aldehyde content, but we have thought that a knowledge of the proportion of esters present would be an aid in forming judgment of these oils. In regard to lemon oil, some work has already been done in this field, and the following data are available:

Unmey and Swinton¹ report on an examination of lemon oil, giving an account of a process which involves the distillation of the terpenes *in vacuo*, removal of the aldehydes from the remaining oil by means of sodium acid sulfite, saponification, and fractional distillation to isolate the alcohols. The statement is made that pure oils contain from 1.2 to 1.4% of esters, calculated as geranyl acetate. We consider the process to be too involved to be a generally useful method of examination, and believe the quantitative separation of the aldehydes by the acid sulfite method to be practically impossible.

Berté states that the saponification number of the evaporation residue of a lemon oil should not exceed "3.5%," a higher figure indicating added fats.²

A. Parrozzani³ has recently published the results of some examinations of "terpeneless" lemon oils. The "terpene-free" oils are distilled with steam, and the aldehydes removed from the distilled oil with acid sulfite, but beyond these statements nothing is said regarding the procedure followed in the ester determination. Parrozzani gives the ester content of five of these concentrated oils, the range being from 26.1% to 37.2%, calculated as linalyl acetate. He believes that the ratio between the ester and the aldehyde content should be useful in judging a terpeneless oil.

II. Material.—The material upon which our experimental work was done consisted, first, of mixtures of known composition, which were made up as follows:

(1)	linalyl acetate	2.5%	citral	4%	limonene	93.5%
(2)	"	"	2.0	"	4	" 94.0
(3)	"	"	1.5	"	4	" 94.5
(4)	"	"	1.0	"	4	" 95.0
(5)	"	"	0.5	"	4	" 95.5

The linalyl acetate, obtained from Fritzsche Bros., had been stored under conditions favorable to its preservation. It showed an ester content of 85.3%. The citral was a fresh sample, purchased from Fritzsche

¹ *Loc. cit.*

² *Boll. chim. farm.*, **43**, 709; through *Chem. Zentr.*, **1904**, II, 1670. The exact meaning of the term "3.5%" is not stated in the abstract. The original has not as yet become available.

³ *Ann. R. Staz. Sperim. Acireale.*, **2**, 86 (1914); abstract *J. soc. chem. ind.*, **34**, 301.

Bros. The limonene was obtained from lemon oils by fractional distillation *in vacuo*, as described below, and it had an apparent ester content, after neutralization, of 0.46%, calculated as linalyl acetate. Considering the fact that practically no limonene remains in the sample after the fractional distillation, the effect of this amount of saponifiable matter on the determination of esters in the mixtures made up with these terpenes is negligible.

Further, experimental work was done upon samples of Sicilian lemon oils taken from regular importations; and upon some samples of terpeneless lemon extracts, partly commercially made, partly prepared in the laboratory.

III. Method.—For the determination of volatile esters, the authors propose the following manipulation:

First, the terpene fraction is removed as follows: 100 g. of the oil are weighed into a 3-bulb Ladenburg flask, the flask hung in a hemispherical iron air bath, connected with a pump producing a vacuum of 2-5 mm., a small flame placed below, regulated to give a slow rate of distillation, (not exceeding 18-20 drops per minute), and the process not disturbed until limonene ceases to come over.

When the automatic stopping of the vacuum distillation has taken place, the flask is connected with a long condenser, and a current of steam passed through until the volume of the distillate reaches 200 cc. This distillation is so regulated as to consume at least 30-45 minutes. The volume of material in the flask is kept as nearly constant as possible by heating with a flame. When the steam distillation is carried out in less time than this, it is almost invariably found that a sufficient amount of less readily volatile material is driven over to produce murkiness and to interfere seriously with the titration. The same effect is observed when the volume of oil with water in the flask becomes too low. When a large volume of water accumulates in the flask, the results appear to be too low, due to incomplete volatilization of the ester. The steam distillates are always found to be slightly acid to phenolphthalein, but no relation between this acidity and the saponification value has been observed.

A concentrated aqueous solution of the theoretical quantity, or an excess of semicarbazide hydrochloride with an equivalent amount of crystalline sodium acetate is now added. This is calculated from the aldehyde content, determined previously by Hiltner's method.¹ When an insufficient amount is used, the end point is not sharp. 100 cc. of 95% alcohol are then added, the mixture shaken around for a few minutes, and allowed to stand for 10-15 minutes, or longer, if convenient. A large bulk of citral semicarbazone usually separates at this point. The solution is then neutralized to phenolphthalein, 50 cc. 0.5 *N* alcoholic KOH added,

¹ U. S. Dept. of Agr., Bur. of Chem., *Bull.* 132, p. 102; *J. Ind. Eng. Chem.*, 1, 798.

and the solution boiled under a reflux for two hours. At the end of this time it is cooled to room temperature without delay, under tap water, and the excess alkali titrated with 0.5 *N* hydrochloric acid. It is necessary to use a much larger quantity of phenolphthalein than in ordinary titrations. Using a 100 g. sample, the number of cc. of 0.5 *N* alkali consumed, multiplied by 0.098 (the value in grams of 1 cc. 0.5 *N* linalyl-acetate), and an empirical factor (see below) gives the percentage of saponifiable matter present, calculated as linalyl acetate.

The above described process, when applied to lemon extracts, takes the following form:

400 g. are distilled slowly from an ordinary side-neck flask until the volume is reduced to 50–75 cc. Steam is then passed through until no more volatile oil comes over. The combined distillates are then treated exactly as the steam distillate in the case of lemon oils, calculating the necessary amount of semicarbazide from the citral value (1 g. citral requires about 0.75 g. semicarbazide hydrochloride).

IV. Experimental.—In the course of our preliminary work certain points were established, to which attention is called. Since it was recognized that aldehydes, on heating with alkalies, tend to resinify, or polymerize, and consequently combine with some alkali, experiments were carried out with a view to their quantitative removal. Neither sodium acid sulfite nor neutral sulfite could be made to serve this end. Precipitation and removal of the aldehydes as semicarbazones was then tried but this failed, as it was found impossible to wash the precipitate completely free of absorbed ester. This was manifest on saponification of the washed precipitate. That the consumption of alkali was due to ester, and not to a splitting of the semicarbazones, was shown by heating with excess of 0.5 *N* KOH, a preparation of pure citral semicarbazone, made from the commercial article in the usual way. Titration of the uncombined alkali showed a negligibly small apparent ester content.

Our experiments prove, then, that if the aldehydes be first condensed with semicarbazide, they do not resinify, and the semicarbazones are not hydrolyzed during the saponification of the esters with alkali, so that *condensation with semicarbazide is recommended as a general procedure as a preliminary to determination of the saponification value, when aldehydes are present.* Much trouble had been encountered, at first, in judging the phenolphthalein end point in the titrations, owing to the extreme murkiness of the solutions, and it was expected that when the aldehydes had been disposed of, the saponification solutions would remain clear and practically colorless. It was soon found, however, that the aldehydes were not alone responsible for our failures; only after the volatile part of the concentrated oil remaining after the vacuum distillation had been distilled out with steam, and the free aldehyde group protected

by condensation, could a satisfactory saponification be effected. It is evident, then, that the nonvolatile, or resinous, parts of the oil must be separated before the determination of the volatile esters is attempted. These resins themselves have a saponification value, as shown by the following experiment: The total nonvolatile matter from 100 g. of one lemon oil weighed 2.6 g. This showed, on saponification, an apparent linalyl acetate content of 1.15 g., or 1.15% of the original oil; calculated to the residue, this was 44%. The end point was very difficult to determine. This material, since it is not volatile either *in vacuo* or with steam, cannot be regarded as either linalyl or geranyl acetates; its composition is by no means clear, and for these reasons we hold that the determination of the esters should be made only in the volatile parts of the oils.

The amount of linalyl acetate, calculated from values obtained upon saponification of the pure ester under the best conditions, was found to be on the average 85.3% of that actually present,¹ while in carrying through our process, the average was 78.4%, indicating a constant loss of about 7% of the ester used in making up the mixture. The range was 77.0–80.3%. The saponification of linalyl acetate was carried out by boiling 1.000 g. of the ester two hours under a reflux with 50 cc. 0.5 *N* alcoholic KOH, cooling at once and titrating back with 0.5 *N* hydrochloric acid to phenolphthalein.

To convert the apparent ester value, then, into a figure which will indicate almost exactly the true content of saponifiable matter, calculated as linalyl acetate, we multiply the former by $100/78.4 = 1.28$.

In Table I are given data relating to a few typical examples taken from thirty-eight experiments on the mixtures of known composition; in Table II, results of the application of the method to the commercial lemon oils mentioned above. The figures are given merely to indicate how closely two successive trials have been made to check; fresh, authentic samples must be collected before limits may be set for the volatile ester content or for its relation to the aldehyde content. In Table III are given some data obtained in work on a few "terpeneless" lemon extracts.

As soon as authentic samples become available, work will be done on orange and other oils as well as on lemon oil, in order to establish limiting analytical figures. Extracts, especially those of the "terpeneless" type, will be prepared from these oils and examined in the same way. The possibility of developing a gravimetric method for the determination of aldehydes, making use of the insoluble semicarbazones is suggested. The authors propose to attempt to distinguish between lemon oil aldehydes and lemongrass citral by investigating the properties of the respective semicarbazones.

¹ According to Barillet and Berthel , equilibrium is reached when 85.5% of pure linalyl acetate is saponified with excess KOH. *Bull. soc. chim. de France*, 1915, 20.

TABLE I.—MIXTURES OF KNOWN COMPOSITION.

No.	Ester content. %	Wt. sample. G.	Vacuum distillation.			Ester found. %	Ester found. % theo- retical.	Ester found × 1.28.
			Pres- sure. Mm.	Temp. of distn. of bulk. °	Time. Hrs.			
34	2.50	100	3	31.0°	4	1.97	78.8	2.52
38	2.00	100	3	36.0°	3½	1.58	79.0	2.02
66	1.00	100	3	..	4½	0.77	77.0	0.99
67	1.00	200	6	0.79	79.0	1.01

TABLE II.—NATURAL LEMON OILS.

No.	Aldehyde content. % citral.	Wt. sample. G.	Vac. distn. Hours.	Ester found. %	Corrected ester content. %	Ratio esters to aldehydes.
54001	5.4	100	3¾	1.32	1.69	0.31
54001	5.4	100	4	1.36	1.74	0.32
53933	4.9	100	4½	1.05	1.34	0.27
53933	4.9	100	2¾	1.08	1.38	0.28
53955	4.8	100	4½	0.99	1.27	0.26
53955	4.8	100	3½	0.97	1.24	0.26

TABLE III.—"TERPENELESS" LEMON EXTRACTS.

No.	Wt. sample. G.	Vol. distillate. Cc.	Ester found. %	Corrected ester content. %
75	400	700	0.11	0.14
79	400	600	0.07	0.09
80	400	600	0.08	0.10

Summary.

The following method, in brief, is suggested for the determination of the volatile saponifiable matter, calculated as linalyl acetate, contained in citrus oils. The terpene fraction is distilled *in vacuo* from a large, say, 100 g. sample, and the remaining volatile oil removed by steam distillation. The aldehydes in the steam distillate are condensed with semicarbazide hydrochloride and the esters determined in the presence of the semicarbazone by saponification with KOH. The process is applicable to the corresponding extracts by distilling off all the readily volatile matter and treating this exactly as the steam distillate obtained in the examination of the oils. The manipulation described in the text should be adhered to.

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A STUDY OF THE CHEMICAL AND PHYSICAL PROPERTIES OF OILS DISTILLED FROM THE VARIOUS PARTS OF THE PLANT ACORUS CALAMUS, L.

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Acorus calamus, L., (Family Araceae) is found in the moderate zones of all the countries in the northern hemisphere, being indigenous to the

¹ Published by permission of the Secretary of Agriculture.