classical series in the Annalen on "Terpene und Campher"[1] Wallach uses the term in this, its broadest sense. In this sense it has also been used recently in an advertisement "Curcumen, Terpen $C_{15}H_{24}$, das neue Cholagogum."[2]

IV. Terpenes $(C_5H_8)_x$ *and Their Derivatives.*—Not only have Wallach's students been dubbed "Terpenkuenstler" even though the material upon which they worked were not hydrocarbons, but related oxygenated compounds, Fr. Heusler in 1895[3] contributed the article "Terpene" to the *Handwoerterbuch der Chemie* in which more space is devoted to related oxygenated compounds than to the hydrocarbons. As late as 1829 Ossian Aschan dedicated his treatise on Naphtenverbindungen, Terpene und Campherarten to Otto Wallach, "dem Altmeister der Terpenchemie." Hence, although in the title he differentiates between terpenes and camphors, he refers to Wallach's special field as terpene chemistry. These two illustrations of rather loose usage might be multiplied.

EXTERNAL EMULSIONS WITH A NEW EMULSIFIER.*

BY L. G. FREEMAN[1] AND E. L. SCHWABE.

The frequency with which prescriptions occur calling for oil, limewater and one or more impalpable powders such as zinc oxide, calamine, etc., presents a problem of finding a method which will give sufficient saponification to completely emulsify all of the oil and suspend these impalpable powders.

A number of series of emulsions were prepared without the incorporation of the impalpable powders, varying in oil content from 15–85%, some two hundred emulsions in all.

Olive oil, being most frequently prescribed, was used with the idea of developing a standard method of procedure, which, with modifications, could be applied to other oils. Twelve series of emulsions were prepared by the bottle method, English and Continental mortar methods, and the electric mixer, with and without added emulsifiers. Observations of separations occurring were made at varying intervals from twenty-four hours to six months. The following key being used to identify the oil–water ratios:

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[1] The same words are used in his book title "Terpene und Campher. Zusammenfassung eigener Untersuchungen auf dem Gebiete der alicyclischen Kohlenstoffverbindungen von Otto Wallach." Leipzig, 1909.

[2] Cover page of *Pharm. Zentralh.* for Dec. 19, 1926.

[3] This article was published in book form in the following year. In the preface thereto the following passage occurs: "Dem Umstande Rechnung tragend, dass die *Chemie der Terpene* (Italics the writers) zur Zeit im Vordergrund des wissenschaftlichen Interesses steht...." The table of contents refers to the following chapters:

Hemiterpene
Eigentliche Terpene
Kohlenwasserstoffe $C_{10}H_{18}$
Kohlenwasserstoffe $C_{10}H_{20}$
Anhang: Glieder der Terpengruppe mit offener Kohlenstoffkette
Sesquiterpene und Polyterpene.

* Section on Practical Pharmacy and Dispensing, A. PH. A., Toronto meeting, 1932.

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	Per Cent.										
Oil	85	75	65	60	55	50	45	40	35	25	15
	A	B	C	D	E	F	G	H	I	J	K
Water	15	25	35	40	45	50	55	60	65	75	85

The results of these series show that where no added emulsifier is used the F or 50–50 ratio produces the greatest amount of emulsification. Tragacanth yields a better emulsion when water is in excess, poorer when the oil is in excess. Increasing the amount of tragacanth does not increase the amount of emulsification. The electric mixer gives a greater amount of emulsion, due to a finer subdivision of the particles, than do the other methods. With the English mortar method acacia yields a greater amount of emulsion than tragacanth.

Using the preceding series as a basis for further investigation, a number of series were now prepared using the same oil–water ratios as before and introducing Triethanolamine (from here on referred to as "*T*") as an added emulsifier to the limewater or distilled water, both with and without the addition of oleic acid.

SERIES NO. 20: OLIVE OIL, LIMEWATER, 2 CC. "*T*," BOTTLE METHOD.

The "*T*" was dissolved in the limewater and the oil added all at once, then vigorously shaken for one minute.

Results: Corresponded to series No. 1, namely, limewater and olive oil, by bottle method.

SERIES NO. 21: OLIVE OIL, DISTILLED WATER, 2 CC. "*T*," BOTTLE METHOD.

Results: Here we have a decidedly different preparation. The F showing twice the amount of separation as that of F-20. The clear separated layer was aqueous. The A of this series gives complete emulsification with no indication of separation on standing six months; whereas the A's of all other series separate fifty per cent in twenty-four hours and seventy-five per cent at the end of six months.

Subseries of A-20 and A-21 were made using decreasing amounts of "*T*" to determine how much was necessary to produce a homogeneous and stable emulsion. The "*T*" was decreased thus: A—2 cc., A1—1 cc., A2—0.5 cc., A3—0.35 cc., A4—0.25 cc., A5—0.20 cc., A6—0.15 cc.

Results: In the A-21 subseries, A, A1, A2 and A3, gave complete emulsification and no separation at the end of six months; A4 separated almost immediately and after six months showed three layers with an emulsified layer of about five per cent of the total volume; A5 and A6 showed no emulsification at all. In the A-20 subseries, A1 separated about 55% at the end of three days, and A2 about 70%. In both cases, 20-A1 and 20-A2 developed into three layer separations at the end of six months. The remaining emulsified layer of A2 was only one-sixth that of A1. The separation into layers of 20-A5 at the end of three days was about the same as at the end of six months; but for 20-A4 and 20-A3, containing larger amounts of "*T*," the separation at the end of three days was proportionately less, while at the end of six months this emulsified layer had contracted into a layer that in each case was proportionately less than that of the weaker "*T*" sample 20-A5.

The results from series No. 1 (limewater, olive oil, bottle method), and the results from series No. 20 (limewater, olive oil, "*T*," bottle method) indicate that they

form two different types of emulsions; one, an oil-in-water, the other a water-in-oil type. The results from the two subseries show that when these two types of emulsions are present in the same preparation, a greater amount of separation occurs than when the emulsion is only of one type. However, it would be necessary to make a more thorough study using 0.1-cc. to 5.0-cc. portions of "*T*" with the various A-K oil–water ratios, to determine which, if any, limewater-"*T*" combination would give us complete emulsification with no separation in a six months' period.

The above limitations suggested the introduction of oleic acid into the formula, which resulted in the following investigations:

SERIES NO. 22: OLIVE OIL, LIMEWATER, OLEIC ACID 5%, "*T*" 2%, BOTTLE METHOD.

(The above percentage figures represent the number of cc. substitution of olive oil by oleic acid and of limewater by "*T*" on a 100-cc. basis.)

Olive oil plus oleic acid is added to limewater plus "*T*" and vigorously shaken for one minute.

Results: Comparable to series No. 21 except that the emulsions were whiter and there was creaming. That is upon separation, instead of the aqueous layer being transparent, as it was in the previous series, it had a light cream color and an opacity like skimmed milk. From C to A the emulsified layer was more cream colored than from D to K. A of this series was perceptibly darker than sample A of series No. 21; and again complete emulsification resulted with no separation in six months.

SERIES NO. 23: OLIVE OIL, DISTILLED WATER, OLEIC ACID 5%, "*T*" 2%, BOTTLE METHOD.

Results: Similar to the previous series No. 22 except that the separated aqueous layer was tan and only slightly turbid. Sample No. 23-A showing a very small amount of separation at the end of six months; whereas the A's of the previous series showed no separation whatever. The oleic acid emulsions were less viscid than those in which it was not used.

A subseries of 23-F was made using varying amounts of oleic acid and adding the water plus "*T*" to the oil plus oleic acid, the other factors remaining the same. Series as follows: F1—2 cc., F2—4 cc., F3—6 cc., F4—8 cc., F5—10 cc., F6—15 cc.

Results: F1 to F4 had the same amount of emulsification which corresponded to 22-F and 23-F; F5 showed slightly more emulsification; F6 showed one-third more emulsification. The separated aqueous layers were pale tan and milky, with the emulsion cream colored. In F1 to F4 these layers were white. This shows that it takes more than 5% of oleic acid to increase the amount of emulsification with 2% "*T*." This series shows that oleic acid is not necessary for complete emulsification of the larger amounts of oil; but does promote the formation of more minute particles which consequently increases the homogeneity and stability of the emulsion.

To find out what effect varying methods of agitation have on "*T*" emulsions, F's of the various series were made with an electric mixer and in the mortar.

Results: Those made with the mixer did not yield a greater volume of emulsified layer and separated just as rapidly as those made by the bottle method. The ones made in the mortar did not yield as great a volume of emulsified layer as either of the others and separated more rapidly.

The possibility of using "*T*" as an emulsifier for other oils was tried using the 50–50 ratio, with the following results: oil of almonds (expressed) gave complete emulsification with 0.35 cc. or more of "*T*." Cotton seed oil gave no emulsification with varying quantities of "*T*" up to 1 cc. Cod liver oil gave complete emulsification with 0.35 cc. or more of "*T*." Castor oil gave complete emulsification with 0.35 cc. or more of "*T*." Liquid petrolatum gave complete emulsification with 0.35 cc. of "*T*" when 5% oleic acid was added.

SUMMARY.

Many oils containing free fatty acids yield stable emulsions with "*T*." As the per cent of oil increases, the amount of emulsification brought about by using "*T*" is increased, 85% oil and 15% water yielding a product which does not separate on six months' standing. When the free fatty acid content of the oil is sufficiently high, stable emulsions can be made with aqueous solutions of "*T*." Oleic acid may be added to an oil when it contains no free fatty acid or an insufficient amount to completely emulsify the oil and produce a stable emulsion with "*T*."

Quick, thorough agitation is necessary in the preparation of these emulsions. If the agitation be too vigorous and too prolonged, as found when the electric mixer is used for longer than one minute, the emulsion tends to break.

The kind of agitation produces some variation in the amount of emulsification. The bottle method yields as stable and homogeneous an emulsion as any of the other methods; and in addition requires less time and incurs no loss of the final product.

Triethanolamine is indicated as an emulsifier for pharmaceutical preparations where an emulsifier is necessary; either as the emulsifying agent or as an added emulsifier.

THE PREVENTION OF RANCIDITY BY MALEIC ACID.

Maleic acid has been found serviceable for preventing rancidity in edible fats and oils. Dr. G. R. Greenbank, of the U. S. Department of Agriculture, who made the discovery, has applied for a public service patent on its use for this and similar purposes; under such a patent, the product can be used freely by anybody, and no one can establish a monopoly.

Dr. Greenbank was led to his discovery in research to find out why some oils and fats kept naturally better than others. He did not succeed in learning this, but did learn that the natural "better keepers" had extremely minute quantities of unidentified organic acids in them. Then he tried adding acids of known composition to oils and fats, and soon found that maleic acid, added in a proportion of one part to ten thousand of the oils to be preserved, would greatly extend the limits of rancidity, the better the quality of the oil the longer it would be preserved by the maleic acid. Further study is being given to the chemistry of maleic acid's efficiency in preventing rancidity.

COBWEBS FOR QUININE IN 1883.

"Cobwebs are the coming remedy as a substitute for quinine, according to Spanish medical authorities. Dr. Oliva, in the *Correspondent Medical*, summarizes 119 cases of treatment by this remedy (telerana is the Spanish name for cobweb), and concludes that it will cure intermittent malarial fever, whether quotidian or tertiary. The dose is 30 grains for adults, 15 for children." *Chemist and Druggist*, Feb. 15, 1883.