electrode which has been presaturated with hydrogen immediately before it is placed in the sample to be investigated. The voltage of the electrode will usually come to a stable reading in 5–15 minutes and remain there for 15–20 minutes or even longer. After this time the electrode usually starts to poison and the voltage drops off. The p_H is calculated from the maximum voltage. There is every indication that this maximum point is of real significance since it can usually be checked within 5 millivolts and when it is considered that these solutions are known to slowly poison the electrodes, this would seem to be good agreement. There are occasional samples which poison an electrode so rapidly that no stable reading can be obtained. The reason for this is still unknown for in all such cases the sample had the same history as others which did not poison the electrodes.

The p_H of tinctures of digitalis, aconite and strophanthus have been determined and found to have the following values.

Tincture of digitalis U. S. P.	5.12–5.77
Tincture of aconite U. S. P.	5.20–5.51
Tincture of strophanthus U. S. P.	5.43
Tincture of ergot (U. S. P. X)	4.97

The p_H of several tinctures of aconite which were known to have been made with acid menstruums were determined and found to have values between 2.32 and 4.53.

Conclusions.—A method has been developed for determining p_H in alcoholic solutions using only the set-up common to most laboratories making such measurements on aqueous solutions which will give stable and reproducible values. Such a method should find wide use in any investigation of the alcoholic extractions or changes in the stability of the tinctures obtained. Some results obtained with tinctures of digitalis, aconite, strophanthus and ergot are given.

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THE EFFECT OF VARIOUS COMPOUNDS ON THE RATE OF DEVELOPMENT OF RANCIDITY IN FATS AND OILS.*

BY WILLIAM J. HUSA** AND LYDIA M. HUSA.

In a previous article (1) by the present authors it was shown that benzoic and cinnamic acids have no effect on the rate of development of rancidity in lard. This work has been extended to other substances.

EXPERIMENTAL METHODS.

The Kreis test (2) was used for detecting rancidity, the odor of the test samples serving as a confirmatory test. The tests were carried out as follows:

Five-cc. portions of oil of sweet almonds, with and without added substances, were placed in special 30-cc. Pyrex glass-stoppered test-tubes, with graduations at the 5-, 10- and 15-cc. levels for convenience in adding the reagents in the Kreis test. The tubes were placed in a water-bath at about 60° and held at this temperature for one hour, with occasional gentle agitation. They were then placed in a rack in a north window. After intervals of one week and two weeks the odor was noted and the entire sample then used in making the Kreis test.

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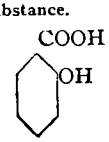
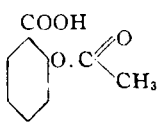
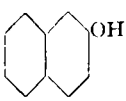
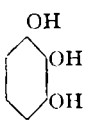
To carry out the Kreis test, 5 cc. of strong HCl (sp. gr. 1.19) was added and the tube shaken vigorously for about 30 seconds. Then 5 cc. of 0.1% solution of phloroglucin in ether was added and the tube shaken as before. If the oil has become rancid, a pink or red color appears in the acid layer, the depth of the color being dependent on the degree of rancidity.

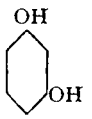
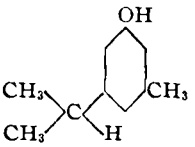
Oil of sweet almonds has an advantage over lard in tests of this kind, in that the solubility of the added substance may be noted. In each case 0.5% of the added substance was employed.

It is possible that certain substances may interfere with the Kreis test by increasing or decreasing the shade of color. An example will best illustrate our method of detecting such effects. Thus a sample of oil of sweet almonds from a freshly opened can gave a colorless Kreis test, which indicated that there was no trace of rancidity. The same oil with the addition of 0.5% salicylic acid also gave a colorless Kreis test. Another sample of oil of sweet almonds from a can which had been opened a few months gave a light pink Kreis test, which indicated that the oil was very slightly rancid. This oil with the addition of 0.5% of salicylic acid gave the same shade of light pink in the Kreis test. These results showed that salicylic acid did not interfere with the Kreis test.

EXPERIMENTAL RESULTS.

The results obtained, using oil of sweet almonds, were as follows:

Substance.	Effect on Kreis test.	Effect on rate of development of rancidity.
Salicylic acid 	None	None
Acetylsalicylic acid 	None	None
Beta-naphthol 	None	None
Liquefied phenol 	None	None
dl-Alanine $CH_3CH(NH_2).COOH$	None	None
Pyrogallic acid 	Interferes by preventing appearance of color	None (judging from odor)
Hydroquinone 	None	Reduces rate of development of rancidity

Resorcinol		Interferes by preventing appearance of color in a slightly rancid oil	None (judging from odor)
Thymol		Color slightly increased	None

The results obtained with lard and hydroquinone were as follows:

	Color Obtained in Kreis Test.	
	After 1 week.	*After 2 weeks.*
Lard	Pink	Cerise
Lard + 0.5% hydroquinone	Light pink	Pink

DISCUSSION OF RESULTS.

Salicylic Acid.—According to Askinson (3), salicylic acid materially counteracts the tendency of fats to become rancid. Lewkowitsch (4) also lists salicylic acid as a preservative of fats. These statements were not substantiated by our experiments, which showed that salicylic acid has no effect on the rate of development of rancidity in oil of sweet almonds.

Acetylsalicylic Acid.—Acetylsalicylic acid has no effect on the rate of development of rancidity.

Beta-Naphthol.—Experiments were carried out with beta-naphthol, because of its reputed value as an anti-oxidant (5). It was found that beta-naphthol has no effect on the rate of development of rancidity.

Phenol.—Moureu and Dufraisse (6) have stated that phenol has a very feeble effect as an anti-oxidant. Our experiments indicate that liquefied phenol has no effect on the rate of development of rancidity.

dl-Alanine.—*dl*-Alanine has no effect on the rate of development of rancidity.

Pyrogallic Acid.—According to Moureu and Dufraisse (6), pyrogallic acid is one of the most active anti-oxidants. Judging from the odor of the test samples, pyrogallic acid has no effect on the rate of development of rancidity. The Kreis test could not be applied in this case because pyrogallic acid interferes by preventing the appearance of the color. This led to the question of whether the pyrogallic acid caused a change in the compounds having a rancid odor, or whether it simply interfered with the reaction with the Kreis reagent. To determine this, two 5-cc. portions of a rancid oil of sweet almonds were placed in glass-stoppered test-tubes and 0.1 Gm. of pyrogallic acid was added to one of the tubes. The tubes were then warmed at 50-60° for 5 or 10 minutes; after this time the rancid odor was the same in both tubes. This result indicates that pyrogallic acid will not remove the rancid odor from a rancid oil.

Since pyrogallic acid is an isomer of phloroglucin, which is used in the Kreis reagent, the question arose as to whether or not there would be a color reaction with a rancid oil if pyrogallic acid in ethereal solution was used in place of the ethereal solution of phloroglucin in making the Kreis test. Tests were made in

this manner and it was found that pyrogallic acid used in place of phloroglucin in the Kreis test gave a colorless acid layer with a slightly rancid oil and a light violet-blue color with a strongly rancid oil. Apparently the color reaction between the rancid compounds and pyrogallic acid is not as delicate as with phloroglucin.

Hydroquinone.—Hydroquinone in the proportion of 1 part to 100,000 parts is said to retard or practically prevent the oxidation of benzaldehyde by air at moderate temperatures (7). Moureu and Dufraisse (6) state that hydroquinone is one of the most active anti-oxidants. In a British patent granted to these investigators (8) the claim is made that the addition of hydroquinone to vegetable oils, such as linseed oil, prevents their turning rancid. Our experiments show that hydroquinone reduces the rate of development of rancidity in oil of sweet almonds. This result indicates that there is at least some basis for the patent claims of Moureu and Dufraisse. Further experiments were carried out by us to determine the effect of hydroquinone on the keeping qualities of lard. The results with the Kreis test indicated that lard alone after one week had reached the stage of rancidity which was reached by lard containing hydroquinone after two weeks. Evidently the addition of 0.5% hydroquinone to lard reduces the rate of development of rancidity about 50%. Further work will be done to determine whether this property of hydroquinone can be applied to the preservation of ointments in a practical way.

Resorcinol.—Resorcinol is said to be of value as an anti-oxidant in benzaldehyde (7) and in rubber (5), but according to Moureu and Dufraisse (6) its action is very feeble. Resorcinol interferes with the Kreis test by preventing the appearance of the color in a slightly rancid oil. Judging from the odor of the test samples, resorcinol has no effect on the rate of development of rancidity.

Thymol.—Smith and Wood (9) have found that thymol inhibits the oxidation of soaps. They have further reported that thymol retards the oxidation of cotton-seed oil and of fatty acids at elevated temperatures. In our experiments, under conditions more comparable to the usual storage of fats, thymol showed no effect on the rate of development of rancidity.

Effect of Metals.—Emery and Henley (10) have shown that metals hasten the development of rancidity in fats. It has commonly been considered that access of both light and air, as well as traces of moisture, is necessary for the development of rancidity in a fat. But Emery and Henley showed that if the fat is in contact with metals, rancidity will develop even if light is excluded.

In our experiments on the effect of metals, 5-cc. portions of oil of sweet almonds in glass-stoppered Pyrex test-tubes were stored for two weeks in a dark cupboard. In some of the tubes, a strip of sheet metal was immersed in the oil. In two weeks, there was no development of rancidity in the oil of sweet almonds alone, or in the oil of sweet almonds in contact with aluminum. The oil in contact with a strip of tinned iron gave a pink color in the Kreis test after two weeks, compared with a barely perceptible pink tinge at the beginning of the experiment. This result indicates that tinned iron accelerates the development of rancidity. It should be noted, however, that the tinned iron strips gave a surface of tin on the sides and iron at the edges. The oil in contact with copper turned bright green and for this reason it was impossible to use the Kreis test in this case.

An experiment was also carried out to determine whether benzoic acid would

have the effect of counteracting the accelerating effect of tinned iron on the development of rancidity. The results indicated that 0.5% of benzoic acid does not alter the rate of development of rancidity of oil of sweet almonds in contact with a strip of tinned iron.

In addition to a further study of the effect of hydroquinone, it is our intention to investigate a number of other substances.

SUMMARY.

1. Hydroquinone reduces the rate of development of rancidity in oil of sweet almonds.

2. The addition of 0.5% of hydroquinone to lard reduces the rate of development of rancidity about 50%.

3. The following compounds have no effect on the rate of development of rancidity: salicylic acid, acetylsalicylic acid, beta-naphthol, liquefied phenol, *dl*-alanine, pyrogallic acid and resorcinol.

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(9) Otto M. Smith and Robert Eri Wood, *Ind. Eng. Chem.*, 18 (1926), 691–4.
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SERTÜRNER MEMORIAL.

A memorial plaque was recently unveiled in the medical clinic of Münster in honor of F. W. A. Sertürner, pharmacist of Eimbeck, the discoverer of morphine, who was born near Paderborn, Westphalia, Germany), in 1783.

SMITHSONIAN SCIENTIFIC SERIES.

The Smithsonian Institution has engaged to prepare a series of twelve books to be known as the "Smithsonian Scientific Series," under the general editorship of the acting secretary. It is the purpose of the series to give pictures of the activities of the whole institution and its branches. The publication is not intended for the specialist nor in any sense is it a collection of monographs, but is rather intended to present those features of the greatest interest to the average intelligent reader with no special training along technical lines. It is expected that the individual books of the series will come out at various intervals during the next two years.

STATE UNIVERSITY IN BRAZIL.

The Rio de Janeiro correspondent of the *Journal of the American Medical Association* writes that the President of the Minas Geraes[1] has signed the law creating a state university. This will include at first four colleges, namely, law engineering, medicine and odontology and pharmacy. The medical school will have an annual endowment of 600,000 milreis (about $72,000).

[1] One of the States of the United States of Brazil.