[CONTRIBUTION FROM THE FOOD INVESTIGATION LABORATORY, BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE.]

THE HYDROGEN NUMBER OF SOME ESSENTIAL OILS AND ESSENTIAL OIL PRODUCTS. I. OILS OF SASSAFRAS, ANISE, FENNEL, CLOVE AND PIMENTA.

BY ALAN R. ALBRIGHT.

Received August 24, 1914.

Introduction.

This paper describes a new method for the examination of certain ethereal oils. It depends on the fact that some unsaturated compounds in such oils are capable of quantitative hydrogenation in a solution of colloidal palladium. S. Fokin[1] suggests a "hydrogen number" for unsaturated aliphatic compounds, using molecular platinum as catalyzer, but states that *no cyclic* unsaturated compound will give this. It has been found that a "hydrogen number," corresponding to the iodine number of fatty oils, may be ascribed to some ethereal oils of the type to be discussed.

Catalyzer.—The colloidal palladium used in this work is a commercial product,[2] but it may not be amiss to describe very briefly its preparation.[3] A solution of a palladium salt is added to a solution of an alkali salt of an acid of high molecular weight, in this case the sodium salt of protalbinic acid (an egg albumin decomposition product). An excess of alkali dissolves the precipitate formed and the solution is said to contain the palladium in the form of a hydrosol of its hydroxide. This solution is purified by dialysis and the hydroxide reduced with hydrazine hydrate. On further dialysis and evaporation to dryness there is obtained a water-soluble product consisting of colloidal palladium and sodium protalbinate in the form of black shining lamellae, which contains about 60% palladium. The sodium protalbinate present in the mixture acts, when the material is in solution, as a "protective colloid."[4]

As is well known, colloids in general are precipitated, "flocked out," by ions (*e. g.*, As_2S_3 by $\overset{+}{H}\overset{-}{Cl}$), due to a transfer of electrical charges, but in the presence of a protective colloid relatively large amounts of electrolytes are necessary to bring this about.

Hydrogenation involving the use of colloidal palladium differs from some other processes of catalytic reduction in that the reaction has not been observed to proceed in the absence of water nor if the proportion of water in the reaction mixture be too small. For instance, in the case of

---

[1] *J. Russ. Phys. Chem. Soc.*, **40**, 700–9 (1908); cf. *Chem. Zentr.*, **1908**, II, 2039; also *C. A.*, **3**, 1009 (1909).

[2] Prepared by Kalle & Co., Biebrich, am/R. Price about $2.40 per gram. See Paal and Hartman, *Ber.*, **43**, 248–9 (1910).

[3] Paal and Amberger, *Ber.*, **37**, 124 (1904); *Chem. Zentr.*, **1904**, I, 572.

[4] Paal and Amberger, *loc. cit.*, see also Skita and Franck, *Ber.*, **44**, 2862 (1911); *Chem. Zentr.*, **1911**, II, 173.

cottonseed oil, a portion of this material showed no absorption of hydrogen on being shaken with a small quantity of powdered colloidal palladium. The same result was obtained whether the oil was suspended in 95% alcohol or dissolved in acetone. On adding 15 to 20% of water to the acetone solution, however, reduction took place at a fairly rapid rate. If this more convenient form of colloidal palladium be not available, a substitute may be prepared as needed in the following way:[1] 0.05 g. palladous chloride (the quantity generally used in our experiments), is placed in the shaking flask described below, followed by 50 cc. of 50% alcohol and 1 or 2 cc. of a 1% aqueous solution of gum arabic (the weight of gum used being about one-fourth the weight of the $PdCl_2$). On shaking this mixture in an atmosphere of hydrogen, the chloride is reduced with formation of a black solution of colloidal palladium, which is rendered stable, *i. e.*, "reversible," by the small quantity of the reversible colloid present, gum arabic. While this solution may be substituted for that of the technically prepared substance, it is actually more expensive, as experiments show that 0.02 g. colloidal palladium costing $0.048 is at least as active as 0.05 g. $PdCl_2$, costing $0.075. Paal's colloidal palladium and palladous chloride contain approximately equal percentages of the metal.

Certain substances are regarded as poisonous with respect to colloidal palladium, for example, formaldehyde contained in impure methyl alcohol is said to be harmful, and allyl isothiocyanate entirely inactivates it, so that mustard oil, although theoretically coming within the category of available experimental material, cannot be treated.

No attempt is made to isolate either the colloidal palladium as such, or the hydrogenated sample, but the palladium may be recovered by evaporating the reaction mixture to dryness, igniting, converting the metal into the chloride and boiling the solution of this to obtain palladous chloride, which may be used in place of colloidal palladium as previously described.

Apparatus.—The apparatus used in this laboratory, which is shown in Figs. 1 and 2, is similar in principle to that devised in the organic laboratory of the University of Göttingen. Its fundamental parts are the camshaft, carrying four eccentrics; the shaking baskets "A," attached to the cams and suspended from pulleys on a supporting rod; the absorption flasks "B," which are placed in the wire baskets; the gas buret connected

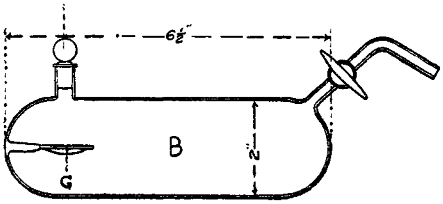


Fig. 1.

---

[1] Skita and Franck, *loc. cit.*

by means of a T tube both with the source of hydrogen and with the absorption flask. Power is supplied by a one-eighth h. p. motor belted to the cam-shaft. When in operation, the shaft has a speed of about 200 revolutions per minute. Hydrogen is supplied from a Kipp generator, or from a steel cylinder and is purified by being passed through a large wash bottle containing alkaline saturated permanganate and is washed with water at each gas buret by a separate wash bottle.

Manipulation.—The manipulation of a reduction is as follows: The air is first displaced from the entire apparatus by passing through it a current of hydrogen, after removing the stopper "C," and lowering the reservoir "D," so that sufficient water remains to form an air trap at the lower bend of the buret. The levels in both arms of the U tube are then equalized at the zero mark. The three-way stopcock "E," is then closed, the stopper "C," which had been replaced during the flushing of the buret with hydrogen, is removed, and 0.02 g. dry colloidal palladium introduced while a current of hydrogen is passing through. Then 50 cc. of 50% alcohol are added, the stopper replaced, the stopcock "F," closed (shown only in photograph) the three-way cock "E," momentarily opened to the air to equalize the pressure in the apparatus with that of the atmosphere, and the flask shaken until no more hydrogen is absorbed. In this way the errors due to (1) absorption of hydrogen by the catalyzer, (2) solubility of the gas in the solvent, and (3) consumption of hydrogen by oxygen dissolved in the solvent, are removed from consideration. The

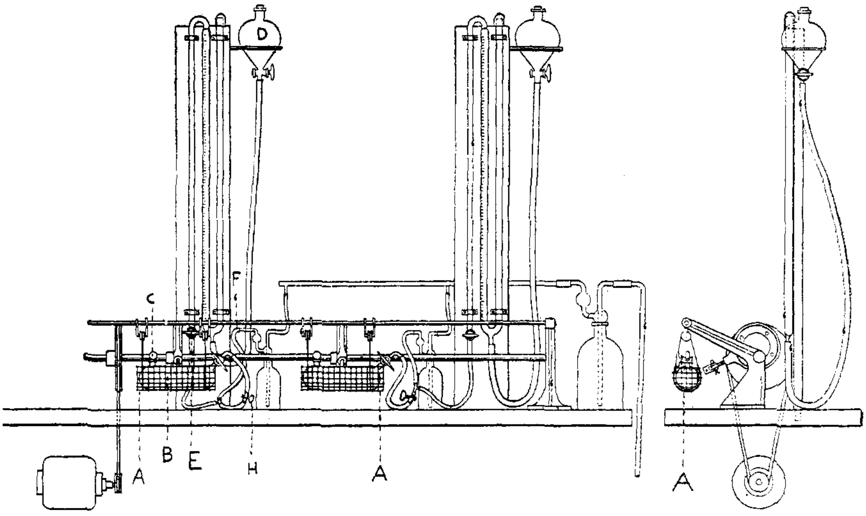


Fig. 2.

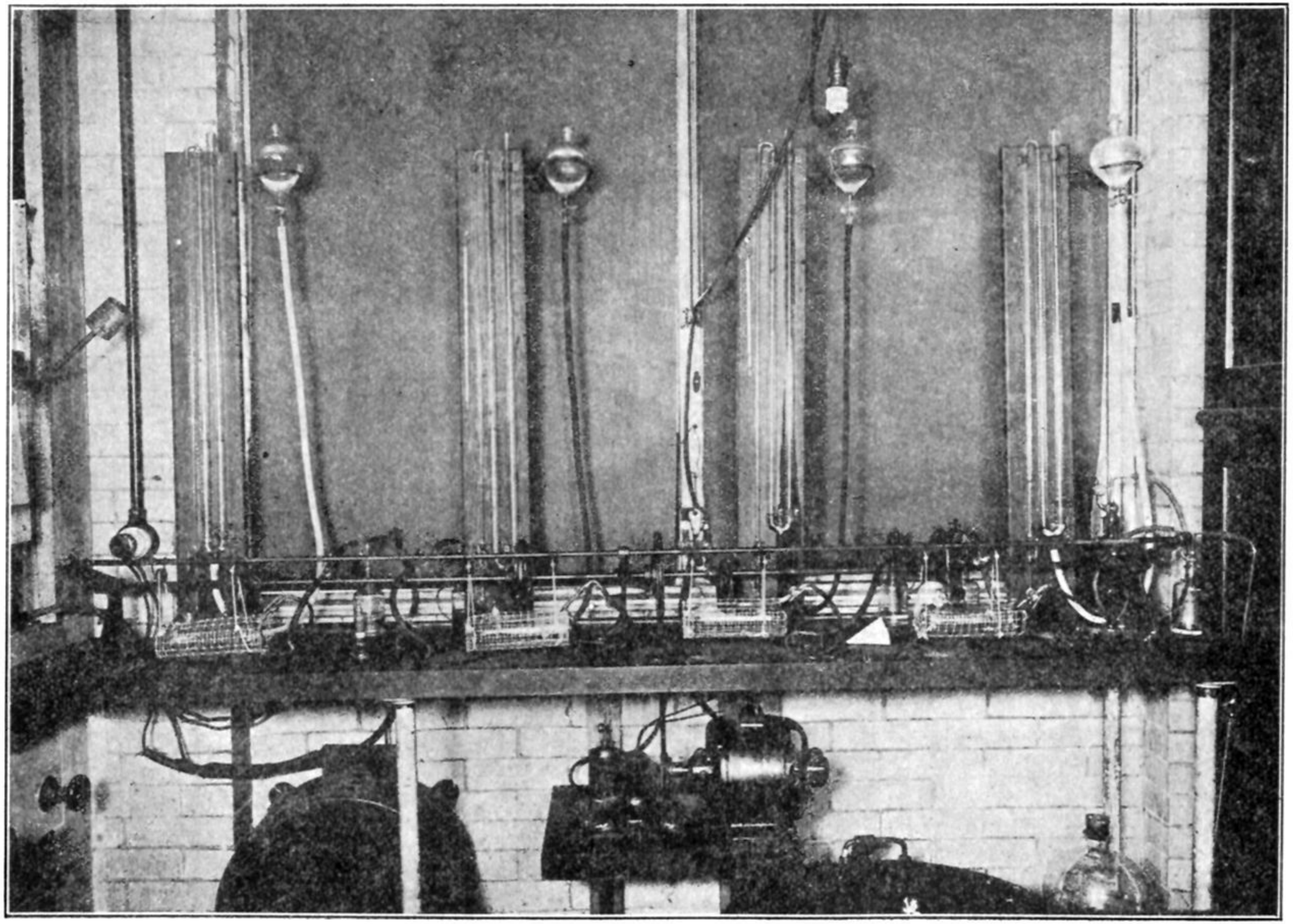


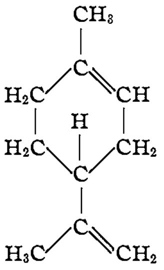
Fig. 3.

buret is again filled to the zero mark with hydrogen and the shaking flask tilted until the palladium solution has drained from the concave "substance table" "G." The substance under investigation is dropped into this table from an oil pipet (weighing bottle),[1] again preventing the entrance of air by maintaining a current of hydrogen through the apparatus. The purpose of this "substance table" is to prevent contact between the catalyzer and substance under examination until the operator is ready to start the experiment. The stopper "C," is replaced, the cock "F," is closed and the cock "E," opened momentarily to the air again. Connection is then made by the same stopcock between the shaking flask and the buret and the machine is at once set in motion. The absorption of hydrogen is carefully watched, maintaining the same water level in each side of the buret by regulating the flow of water from the reservoir. When the reaction is finished, a decided and abrupt decrease in the rate of absorption occurs. On the accuracy of the observation of this point depends the accuracy of the determination. The end point may readily be found otherwise by noting the buret reading at frequent intervals, *e. g.*, every 15 seconds, and plotting volume against time on coördinate paper, when the break in the resulting curve will give the desired result. This point was found in each of the cases to be described by drawing a straight line through the first points, then connecting with a smooth curve those points which lie at the right. The juncture of the straight line representing the main reaction, with the curved line representing absorption of hydrogen by secondary substances, is taken as the end point. The sample weight should be so adjusted that 100 cc. or less of hydrogen will be needed, but in case more than one buret of the gas is to be absorbed, the procedure is as follows: First, the reading is noted and the clamp "H," closed (without interrupting the shaking); then the reservoir is lowered and the cock "F," opened until the water in the graduated branch of the U tube is forced by the pressure of hydrogen from the cylinder down to the level of that in the other and then closed, again reading the buret. The reservoir is hung in the hook, an amount of water equal to about twice the quantity of hydrogen which has been absorbed during the time of refilling the buret, (roughly calculated from the previously observed rate of absorption) is allowed to enter the right arm, and the partial vacuum which has been formed in the shaking flask is released when the clamp "H," is opened. The levels in the two arms of the buret are equalized and the absorption continued to completion.

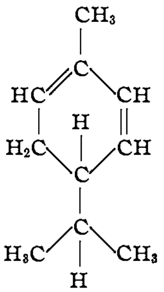
Application.—Every essential oil contains at least small quantities of unsaturated substances, consisting, for example, of one or more terpenes, such as limonene, or phellandrene,

---

[1] Devised by H. S. Bailey of this laboratory.

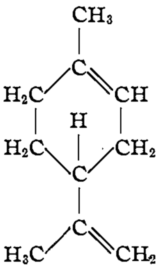


Limonene.

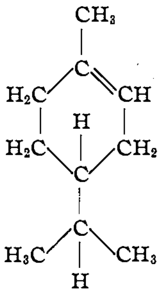


Phellandrene (α).

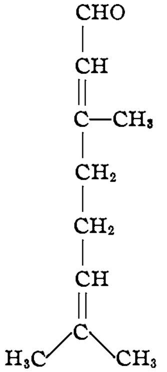
and theoretically a measure of the total "degree of unsaturation" might present a factor useful in judging the purity of the product. Not all double bonds, however, are hydrogenated with equal ease, owing to effects of molecular configuration, and some are only very slowly attacked by activated hydrogen. For example, limonene is first reduced to carvomenthene,[1] citral to citronellal,[2] carvoxime to carvotanacetoxime,[3] the



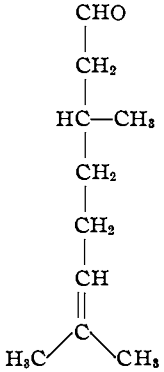
Limonene.



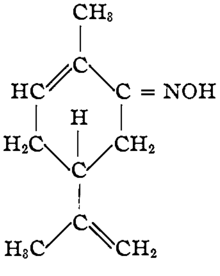
Carvomenthene.



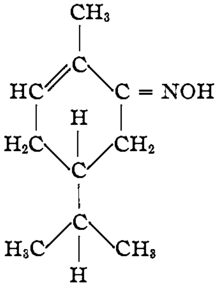
Citral.



Citronellal.



Carvoxime.



Carvotanacetoxime.

---

[1] With Pt black as catalyzer; Vavon, *Chem. Zentr.*, **1914,** I, 1506; with CuO as catalyzer: Ipatieff, *C. A.*, **5,** 891 (1911).

[2] Skita, *Ber.*, **42,** 1627 (1909); cf. *Chem. Zentr.*, **1909,** I, 1931; also *C.A.*, **3,** 2159 (1909).

[3] Albright, "Inaugural Dissertation," Göttingen, **1912**; Wallach and Albright, *Ann.*, **403,** 73 (1914).

second bond in each case requiring considerably longer treatment for complete saturation.

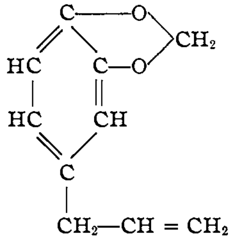
Thus it is seen that the application of a quantitative method in such cases may be attended by unsatisfactory results, in that far too much time may be required for a determination, with possible attendant errors of changing atmospheric temperature and pressure.

Some oils, however, contain compounds which are completely and very rapidly reduced, and it is with oils of this type that the present paper deals. Most notable are those containing a constituent which has within its molecule an allyl or propenyl group, as the double bonds in such groupings are generally capable of very rapid hydrogenation. (Allyl isothiocyanate mentioned before is an exception.) In fact, some compounds of this type are so rapidly reduced that, when an oil containing one of them is under examination, the reaction seems to take a selective course, in that these bonds are quantitatively saturated before those in other configurations are attacked to more than a slight extent. As a matter of fact, however, the reaction is not to be considered rigidly selective, and it is in this fact that the principal error of the determination lies. Nevertheless, in most cases the change in velocity of hydrogen absorption, after the allyl or propenyl group has been saturated, is sufficiently abrupt so that there is no mistaking the end point of the reaction. It is the quantity of hydrogen absorbed in this first and most vigorous action that fixes the "hydrogen number" of the oil. In other words, the hydrogen number of an oil is the number of cc. of hydrogen, reduced to the volume it would occupy at 0° and 760 mm. pressure, which are absorbed by 1 g. of the material in question *during the above described period of most rapid absorption of the gas*. This quantity has been found to be characteristic of the several oils named, and gives a direct measure of the proportion of the active constituent present. For example, from the hydrogen number of clove oil the percentage of eugenol may be readily calculated by multiplying by the factor 0.0073, the weight of eugenol equivalent to 1 cc. of hydrogen. The results are generally slightly too high because of the absorption of hydrogen by secondary substances in addition to that due to the main reaction. By using an appropriate factor weight the buret reading, reduced to standard conditions, will give the percentage direct of these substances, of course with the same qualification regarding error.

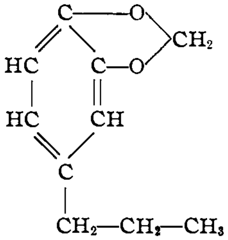
The method of procedure in the working out of the hydrogen number and of the estimation of the principal constituents of the oils under consideration was as follows: first, the active constituents of the oils, namely, safrol, anethol, and eugenol, were prepared in as pure a condition as possible and hydrogenated, in order to prove that they may be quantitatively reduced, and that the break in the curve showing the absorption rate, which is apparently a straight line during the main reaction, actually represents the complete saturation of the one active double bond in each compound. Then an imitation oil was prepared, made up of the active constituent mentioned, in the approximate proportion in which it occurs in the natural oil, while the remaining percentage was represented by pure limonene. Limonene itself absorbs hydrogen fairly rapidly, and was chosen from among other terpenes for that reason, so that as severe a test as possible might be made. Finally, samples of commercial oils were subjected to the same process.

Experimental.

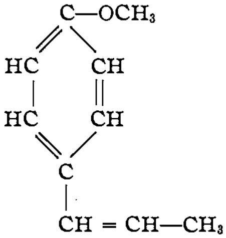
The Reduction of Safrol.—A commercial sample of safrol was redistilled; b. p. 760 mm., 236.0° (mercury entirely in vapor). This substance is reduced to dihydrosafrol with extreme ease. The speed of reaction and sharpness of the end point are remarkable. One-tenth gram colloidal palladium dissolved in about 40 cc. 50% alcohol was saturated with hydrogen, then 4.63 g. safrol were introduced. Absorption began as soon as agitation was commenced, proceeded at a constant rate and ended very abruptly. In ten minutes 720 cc. of hydrogen measured at 22° and



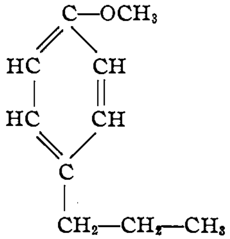
Safrol.



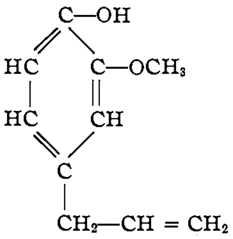
Dihydrosafrol.



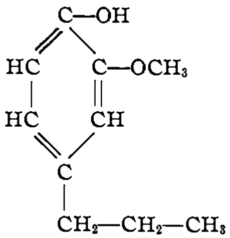
Anethol.



Dihydroanethol.



Eugenol.



Dihydroeugenol.

758 mm. had been absorbed. This is equivalent to 632 cc. at 0° and 760 mm., whereas 4.63 g. safrol should theoretically absorb 641 cc. The reaction product was isolated by distilling with steam, dried with fused calcium chloride and distilled under ordinary pressure, b. p., 234.3–234.5° (mercury entirely in vapor).

0.2026 g. of substance gave 0.1375 g. H_2O and 0.5461 g. CO_2.

Calculated for $C_{10}H_{12}O_2$: H = 7.3, C = 73.2; found: 7.6, 73.5.

Specific gravity 15.6°/15.6° = 1.0759, n_D 15.6° = 1.5228; M. R. = 46.60; calculated = 46.1.

Dihydrosafrol is a colorless oil, stable several minutes toward dilute alcoholic permanganate; quite stable toward dilute aqueous permanganate. The odor is very similar to that of safrol.

Since the work upon which this paper is based was begun, there has appeared an article by Ipatieff[1] in which are described the reductions of anethol, eugenol, and safrol with nickel and hydrogen under about 50 atm. pressure and at from 92° to 95°. The preparation of reduction products for the purpose of analysis has been limited to safrol, since the author's results agree with those of Ipatieff, and since there is every reason, from theoretical and experimental considerations, to assume that the reactions, in the case of anethol and of eugenol, proceed normally as indicated in the above formulas.

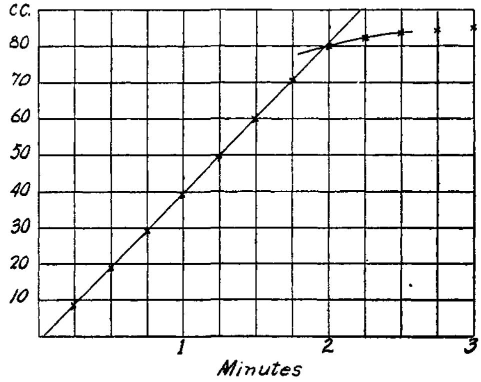


Fig. 4.—Safrol.

Fig. 4 gives a typical curve showing the rate of absorption of hydrogen by safrol. The raw material was a sample of commercial safrol, "Pure U. S. P." This was frozen and pressed out, then distilled under 763 mm. pressure, b. p., 236.3–236.6° (mercury entirely in vapor).

As described before, 0.02 g. colloidal palladium with 50 cc. 50% alcohol were saturated with hydrogen in the shaking flask, after which 0.5119 g. of the substance was introduced. The hydrogen was measured at 24.5°, 766.5 mm. The break in the curve occurs at 80.0 cc., equivalent at 0°, 760 mm. to 69.4 cc., whereas the theoretical absorption is 70.7 cc. Hydrogen number, 135.6; safrol = 98.3%. Each of a number of reductions of safrol gave a result 1 to 2% too low, indicating the probable presence of some much less active substance difficult to separate from safrol.

Fig. 5 shows the rate of absorption of hydrogen by pure limonene from

---

[1] *Ber.*, **46**, 3589 (1913); cf. *Chem. Zentr.*, **1914**, I, 140.

lemon oils, redistilled several times over sodium. The catalytic reagent consisted, as in each of the cases to be described, of 0.02 g. colloidal palladium in 50 cc. 50% alcohol. The sample weighed 0.0390 g. and the gas was measured at 25°, 766 mm.

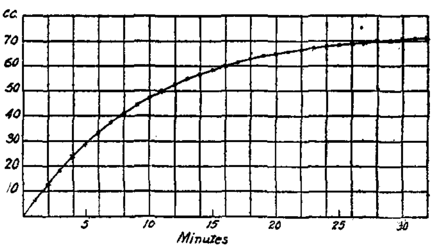


Fig. 5.—Limonene.

Fig. 6 represents the reduction of a factitious sassafras oil, a mixture of 4.000 g. redistilled commercial safrol and 1.000 g. limonene. The quantity taken was 0.561 g. and the break in the absorption curve occurred at 73.7 cc. measured at 26.5°, 765.5 mm. At 0°, 760 mm. this is equivalent to 62.8 cc., giving a hydrogen number of 111.9. Eighty per cent. of 0.561 g. or 0.449 g. safrol at 0°, 760 mm. should absorb 62.2 cc., the error being due primarily to the 20% of limonene present. The proportion of safrol calculated from the absorption is 81.1%.

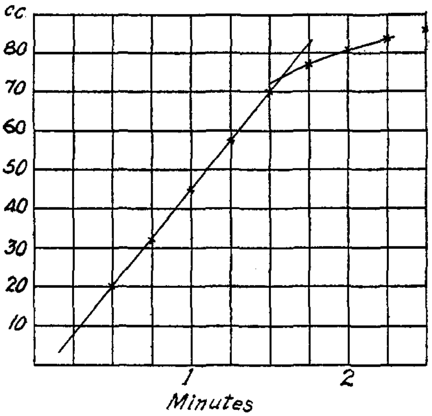


Fig. 6.—Imitation Sassafras Oil.

Fig. 7 represents the hydrogenation of an authentic sassafras oil. Curve 1 gives the result obtained using 0.4261 g. oil, Curve 2, using 0.5071 g. No. 1 absorbed 51.0 cc., No. 2 60.0 cc., each measured at 25°, 763.4 mm. At 0°, 760 mm., absorption by No. 1 would have been 43.9 cc., giving a hydrogen number of 103.1, and a safrol content of 74.8%; by No. 2, 51.7 cc., giving 102.0 as the hydrogen number, and 74.0% as the safrol content.

Fig. 8 shows the course of a reduction of pure anethol, prepared by freezing and pressing out a sample of commercial anethol. The quantity taken was 0.4417 g., the sharp break in the absorption curve coming at 79.2 cc. measured at 28°, 762.4 mm. This is equivalent at 0°, 760 mm. to 66.5 cc. Theory requires an absorption of 66.8 cc. at 0°, 760 mm. Hydrogen number, 150.5; anethol = 99.6%.

Fig. 9 represents the reduction of an imitation anise oil, made of 8.000 g. pure anethol and 2.000 g. pure limonene. No. 1 shows the result obtained with 0.4180 g. of the mixture. The break occurs at 61 cc. measured at 24.5°, 759 mm. This is equivalent at 0°, 760 mm. to 52.3 cc., giving a hydrogen number of 125.1, and an anethol content in the oil of 82.4%. For No. 2, 0.3220 g. was taken. The break is at 47.5 cc. measured under the same conditions as for No. 1, equivalent at 0°, 760 mm., to 40.9 cc. Hydrogen number, 127.0; anethol = 83.7%.

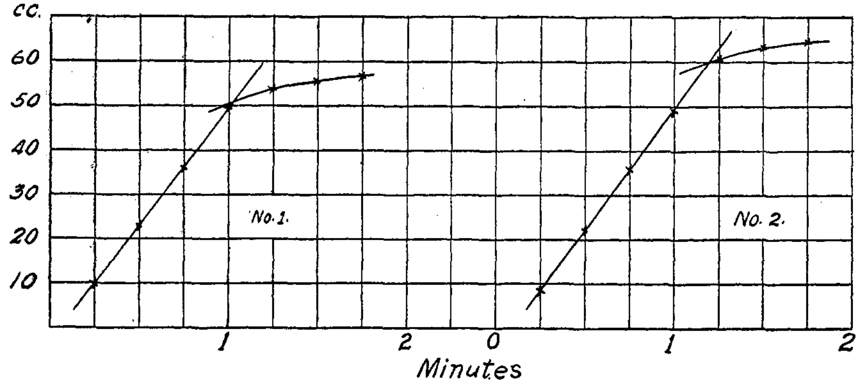


Fig. 7.—Authentic Sassafras Oil.

Fig. 10 shows the results obtained with a commercial anise oil. For No. 1, 0.4109 g. was taken. The end point is at 61.1 cc. measured at 26°, 756 mm., equivalent to 51.7 cc. at 0°, 760 mm., giving 125.8 as the hydrogen number, and 82.9% as the anethol content. For No. 2, 0.4019 g. oil was used, the end point occurring at 60.6 cc. measured under the same conditions as No. 1, equivalent to 51.2 cc. at 0°, 760 mm. Hydrogen number, 127.3; anethol = 83.9%.

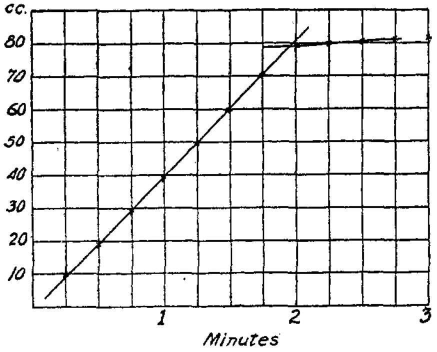


Fig. 8.—Anethol.

Fig. 11. A representative commercial fennel oil. No 1: 0.5378 g. absorbed 62.0 cc. at 22°, 764.4 mm.,

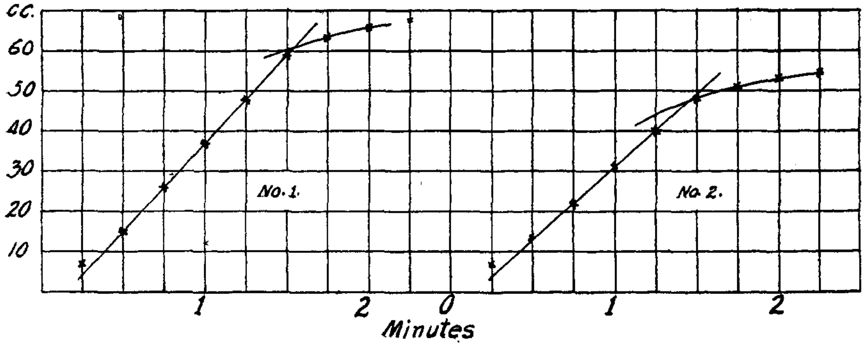


Fig. 9.—Imitation Anise Oil.

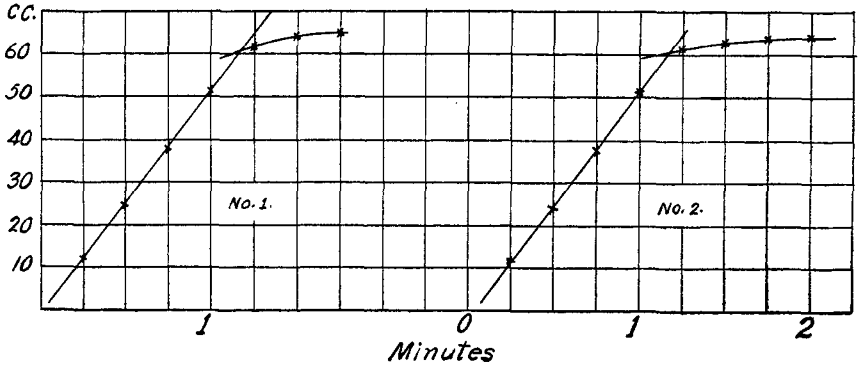


Fig. 10.—Commercial Anise Oil.

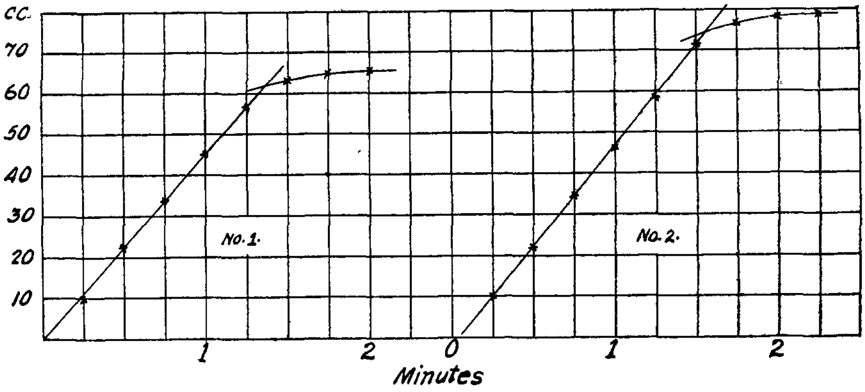


Fig. 11.—Commercial Fennel Oil.

equivalent to 54.4 cc. at 0°, 706 mm., giving 101.3 as the hydrogen number, which represents 66.8% anethol. No. 2: 0.6330 g. at 23°, 764.4 mm., absorbed 74.5 cc., equivalent to 65.0 cc. at 0°, 760 mm. Hydrogen number, 102.7; anethol = 67.7%.

Fig. 12 represents a reduction of eugenol. The raw material was a commercial eugenol, "Pure U.S. P." It was redistilled, b. p., 13 mm., 150–152° (uncor.). 0.4769 g. absorbed 77.7 cc. at 30°, 762.7 mm., equivalent to 64.1 cc. at 0°, 760 mm. Theoretical absorption, 65.1 cc. Hydrogen number, 134.4; eugenol = 98.3%.

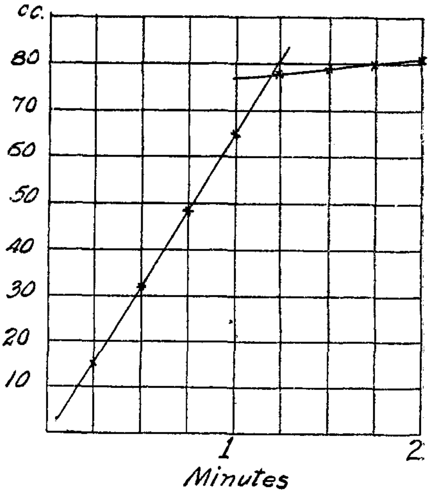


Fig. 12.—Eugenol.

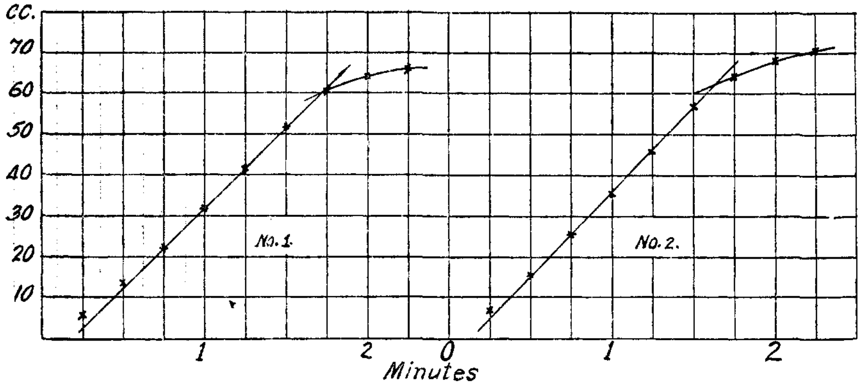


Fig. 13.—Imitation Clove Oil.

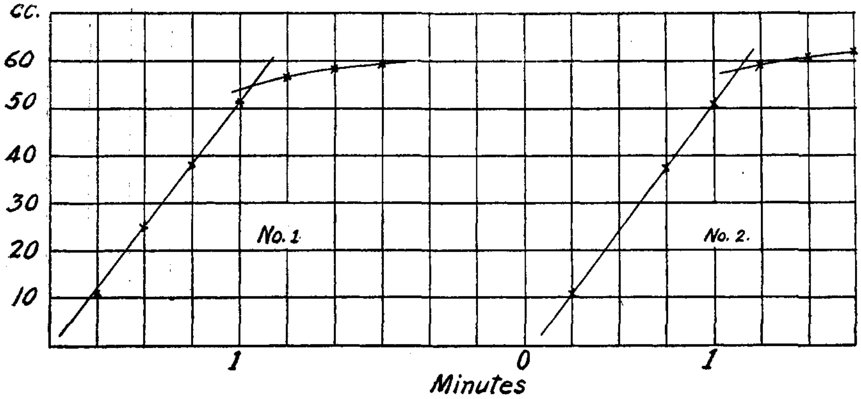


Fig. 14.—Commercial Clove Oil.

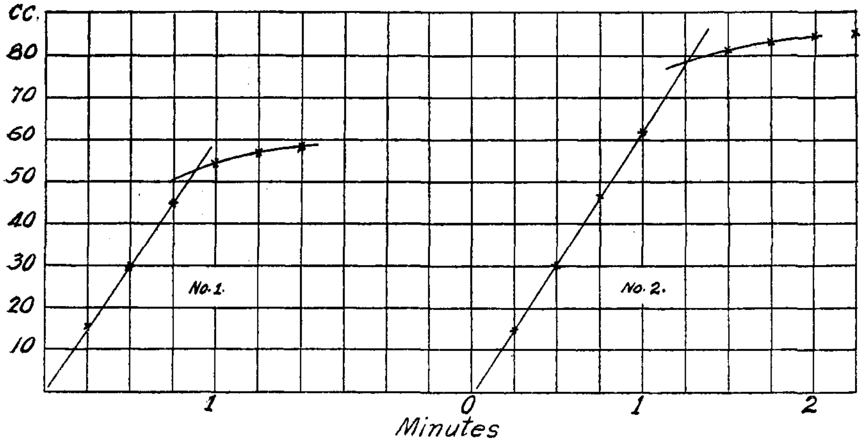


Fig. 15.—Commercial Pimenta Oil.

Fig. 13 shows results obtained on hydrogenating a mixture of 8.000 g. redistilled eugenol and 2.000 g. limonene. No. 1: 0.4620 g. absorbed 60.2 cc. at 24°, 765 mm., equivalent to 52.3 cc. at 0°, 760 mm. Hydrogen number, 113.2; eugenol = 82.8%. No. 2: 0.4806 g. absorbed 62.8 cc. under the same conditions, equivalent to 54.5 cc. at 0°, 760 mm., giving 113.3 as the hydrogen number, which represents 82.8% eugenol.

Fig. 14 shows the results of two experiments with a commercial clove oil. For No. 1, 0.4104 g. was taken, which absorbed 55.0 cc. at 26°, 763 mm., equivalent to 47.0 cc. at 0°, 760 mm. Hydrogen number, 114.6; eugenol = 83.8%. For No. 2, 0.4339 g. oil was used. The absorption at 27°, 763 mm. was 58.3 cc., equivalent to 49.5 cc. at 0°, 760 mm. Hydrogen number, 114.0; eugenol = 83.3%.

Fig. 15 represents reductions of pimenta oil. For No. 1, 0.4592 g. of a representative commercial oil was taken, which absorbed at 27°, 763 mm., 53.0 cc., equivalent to 44.9 cc. at 0°, 760 mm. Hydrogen number, 97.8; eugenol = 71.5%. For No. 2, 0.6830 g. of the same oil was used. Under the same experimental conditions there were absorbed 78.7 cc., equivalent to 66.8 cc. at 0°, 760 mm. Hydrogen number, 97.8; eugenol = 71.5%.

The values for the vapor pressure of the solvent (50% alcohol), used in calculating these results were interpolated between figures published by Doroschewski,[1] and are given in Table I.

TABLE I.

Temperature.	V. p. 50% alcohol in mm. mercury.	Temperature.	V. p.
22.0	42.7	26.0	52.5
22.5	43.8	26.5	54.0
23.0	45.0	27.0	55.5
23.5	46.2	27.5	57.0
24.0	47.4	28.0	58.8
24.5	48.5	28.5	60.5
25.0	49.7	29.0	62.6
25.5	50.9	29.5	64.4
..	..	30.0	66.8

Experiments carried out in this laboratory indicate that the effect of either the catalyzer or oil upon the vapor pressure of the alcohol is negligible.

The results of the above described experiments are given in Table II.

It is planned to obtain a number of additional authentic samples of these and of other oils, so that this table may be amplified and limits for the hydrogen numbers set. It is further our intention to adapt the method to those materials which at present seem to offer greater difficulty, and to devise a simpler and less expensive form of apparatus which may aid the method in finding commercial application.

---

[1] *Z. physik. Chem.*, **73**, 192 (1910).

TABLE II.

Figure.	Substance.	Hydrogen number.	Per cent. of active constituent.	Theoretical per cent. of active constituent.
3..........	Safrol	135.6	98.3	100.0
4..........	Limonene	...	..	...
5..........	Imitation sassafras oil	111.9	81.1	80.0
6..........	Authentic sassafras oil	103.1	74.8	...
		102.0	74.0	...
7..........	Anethol	150.5	99.6	100.0
8..........	Imitation anise oil	125.1	82.4	80.0
		127.0	83.7	80.0
9..........	Commercial anise oil	125.8	82.9	...
		127.3	83.9	...
10..........	Commercial fennel oil	101.3	66.8	...
		102.7	67.7	...
11..........	Eugenol	134.4	98.3	100.0
12..........	Imitation clove oil	113.2	82.8	80.0
		113.3	82.8	80.0
13..........	Commercial clove oil	114.6	83.8	...
		114.0	83.3	...
14..........	Commercial pimenta oil	97.8	71.5	...
		97.8	71.5	..

WASHINGTON, D. C.

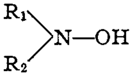
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

THREE ISOMERIC ETHYL SECONDARYBUTYL HYDROXYLAMINES.

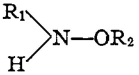
BY LAUDER WILLIAM JONES AND LEONORA NEUFFER.

Received July 31, 1914.

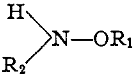
By the substitution of two different groups for hydrogen in hydroxylamine, three isomeric compounds are possible and may be represented by the following general formulas:



A.



B.



C.

Compounds of the type A, β,β-derivatives,[1] were first prepared by Bewad.[2] The first representative of types B and C, α,β-derivatives, was the α-benzyl-β-ethyl derivative prepared by Behrend and Leuchs[3] in 1890. Since then no compounds of the α,β type containing two different radicals were described until Jones,[4] in 1907, prepared two isomeric compounds, *viz.*, α-ethyl β-methyl- and α-methyl-β-ethyl hydroxylamines.

It is the purpose of the present paper to describe the preparation and properties of two new α,β-dialkyl hydroxylamines, which are isomeric

---

[1] In this paper α = attached to O; β = attached to N.

[2] Bewad, *Ber.*, [1] 479 (1888); *J. russ. phys. Chem. Soc.*, **32**, 420 (1900).

[3] Behrend and Leuchs, *Ann.*, **257**, 237 (1890).

[4] Jones, *Am. Chem. J.*, **38**, 253 (1907).