That portion of the oil (79 g.) which was soluble in sulfite had a caraway-like odor, b. p. 92–96° (9 mm.) and formed a semicarbazone with well defined m. p. 148–161°.

α-Phellandrene and Selenious Acid.—Two hundred grams of phellandrene in 400 cc. of alcohol, was treated as above with 160 g. selenious acid in 800 cc. alcohol; solution heated for 24 hours; precipitated selenium, 53 g.; quantity of oil from steam distillation, 135 g.; non-volatile with steam, 96 g.

On fractionating first, distillate was obtained boiling up to 80° (11 mm.), $n_D^{16°}$ 1.492: had a cymene-like odor; the main fraction consisted of a colorless oil b. p. 80–98° (8 mm.), which on further fractionation boiled at 68–70° (0.8 mm.). It formed a semicarbazone of m. p. 207–211° and proved to be the semicarbazone of cumaldehyde.[8] The m. p. of the mixture of this substance and a standard preparation showed no depression.

Piperitone and Selenious Acid.—Fifty grams of piperitone dissolved in 10 cc. of alcohol was treated with 40 g. of selenious acid in 200 cc. of alcohol. Heated twenty-four hours, precipitated selenium filtered off; quantity of oil from steam distillation, 39 g., b. p. 79–82° (0.8 mm.), was nearly completely soluble in sodium hydroxide, could be precipitated from the latter with acids, and then had a b. p. 110–113° (11 mm.) after which it solidified to a crystalline cake m. p. 47–49°. The m. p. of this substance mixed with thymol showed no depression.

(8) St. Warunis and Lekos, *Ber.*, **43**, 654 (1910).

Summary

Δ-1-Menthene oxidized with selenious acid gave carvotanacetone; Δ-3-menthene gave a ketone which by means of derivatives could be shown to be Δ-3-menthene-5-one. As by-products oxides of the menthenes were obtained. α-Phellandrene and piperitone were not only oxidized, but also dehydrogenated by the same oxidant to aromatic compounds, and yielded, respectively, cumaldehyde and thymol.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, TEACHERS COLLEGE, COLUMBIA UNIVERSITY]

Larger Yields of Crystalline Antineuritic Vitamin

BY ROBERT R. WILLIAMS, ROBERT E. WATERMAN AND JOHN C. KERESZTESY

The isolation of the antineuritic vitamin has been reported by several groups of workers.[1] Crystalline hydrochlorides of very similar characteristics having the property of curing or preventing polyneuritis in rats, pigeons or rice birds in doses of the order of 1 to 10 micrograms have been obtained from rice polish, bakers' yeast and brewers' yeast by a number of independent groups of workers using a variety of procedures. The chemical study of this hydrochloride is obviously justified even though one may entertain doubts that it represents the fully isolated vitamin. It is the object of this paper to record the results of our recent efforts to obtain the substance in quantity for purposes of further investigation.

The progress of isolation has been gaged at every step by injection tests on polyneuritic rats according to the method of M. I. Smith.[2] The experience of this Laboratory with this method is recorded elsewhere.[3] We have attempted by such tests to trace and progressively eliminate the losses which we believe occur in the course of all fractionation schemes and thus have evolved the following procedure of isolating the crystals. It produces several fold larger yields than heretofore reported.

(1) B. C. P. Jansen and W. F. Donath, *Mededeel. Dienst Volksgezondheid Nederland. Indië*, pt. 1, 186 (1926); A. Windaus, *Nachrichten v. der Gesell. der Wissenschaften zu Göttingen*, 209 (1932); S. Ohdake, *Proc. Imp. Acad. Tokyo*, **7**, 102 (1931); A. Seidell and M. I. Smith, THIS JOURNAL, **55**, 3380 (1933); W. K. Kinnersley, J. R. O'Brien and R. A. Peters, *Biochem. J.*, **27**, 232 (1933).

(2) M. I. Smith, *U. S. Pub. Health Repts.*, **45**, 116 (1930).

(3) R. E. Waterman and M. Ammerman, to be published shortly.

Preparation of Activated Fullers' Earth

Our raw material, rice polish, has been assayed by boiling 25 g. of the polish three times with 100 cc. of 70% methyl alcohol acidulated to *P*H 4.5 and filtering. The combined extracts are evaporated *in vacuo* to 25 cc. volume. This solution is filtered, neutralized and injected. Repeated tests by this method on several lots of polish have shown that the extract of 0.25 g. of polish represents the minimum curative dose for rats. The activity of rice polish may therefore be taken as about 4000 doses per kilo.

On the large scale 150 to 200 kilos of polish are mixed with 4000 liters of water in a wooden tank equipped with a stirrer. The suspension is brought to *P*H 4.5 by addition of sulfuric acid; 10 liters of toluene are added to prevent bacterial action, the mixture is stirred for five to six hours and allowed to settle for forty-eight hours. About 3000 to 3500 liters of clear liquid is pumped off and the remaining mass of wet polish is stirred up again with the addition of water to replace the extract withdrawn. After another stirring and a settling period the second extract is drawn off as before. In the meantime, the first extract has been stirred for an hour with 4 kilos of fullers' earth for each 100 kilos of polish taken. The fullers' earth is allowed to subside and the clear extract

which is devoid of detectable activity is discarded. The fullers' earth is now stirred with the more dilute second extract and allowed to subside. This serves to wash the fullers' earth somewhat and also to recover the lesser amount of vitamin in the second extract. After the second extraction the thick porridge of rice polish is discarded. Such spent polish when repeatedly extracted with boiling 70% alcohol as above described yields less than 500 doses per kilo.

The resulting activated fullers' earth has been tested by feeding young rats on a B_1 free but otherwise adequate diet with graduated addenda of fullers' earth. A daily addendum of 10 mg. is sufficient to prevent polyneuritis and induce an average growth of 0.8 g. per day; 15 mg. raises the rate of growth to 1.0 g. per day. The activated fullers' earth contains no appreciable amount of B_2. With a 15-mg. addendum of the fullers' earth without B_2 supplement growth ceased and symptoms of B_2 deficiency developed within sixty-five days.

Extraction of Activated Fullers' Earth

Barium hydroxide has been used to extract the vitamin from the fullers' earth by most workers. This we have found to be very inefficient, no more than 50% of the vitamin being recoverable under the most favorable conditions by use of this reagent. The loss is due primarily to retention of activity by the fullers' earth suspended in barium hydroxide solution. We have therefore made use of quinine sulfate[4] solution to displace the vitamin from fullers' earth. The following comparative experiments, illustrative of many others, show the advantage of this reagent.

Sixty grams of activated fullers' earth was stirred with water and barium hydroxide was added to alkalinity to tropaeolin O. This was repeated four times with 250 cc. of water each time. Each filtrate was promptly freed of barium by addition of sulfuric acid to P_H 5.0. The combined extracts amounting to 1 liter were tested by injection. The total activity of the extract was found to be 1000 doses.

Sixty grams of the same fullers' earth was extracted by boiling for one-half hour with 300 cc. of water containing 40 g. of quinine sulfate per liter acidulated faintly to Congo Red with sulfuric acid. The extract was filtered hot and the remaining fullers' earth was extracted again with 200 cc. of the acid quinine sulfate and a third time with 100 cc. The combined extracts were cooled, neutralized with baryta, filtered from quinine sulfate and tested by injection in the same manner; 4600 doses were found to be present.

Accordingly the foregoing method has been adopted as a step in the isolation procedure on a large scale. For this purpose the amount of quinine used in the second and third extractions is somewhat reduced for the sake of economy; 30 kilos of activated fullers' earth together with 6 kilos of quinine sulfate are suspended in 50 liters of water in a 200 liter wooden tank and sulfuric acid is added to faint acidity to Congo Red. The mixture is brought to a boil by direct injection of steam through a hose with addition of further water as necessary to bring the final volume to 170–180 liters. As soon as the liquid boils the steam hose is removed and the suspension is allowed to settle for an hour. The clear liquid is siphoned off while still hot and the more fluid upper layers of fullers' earth are transferred to Buchner funnels to suck off the remaining liquid as far as possible.

The fullers' earth taken out is returned to the tank and the whole is again digested with water with the addition of 2.1 kilos of quinine sulfate, the necessary sulfuric acid and water and steam to make a total volume of 120 liters when hot. The second extract is withdrawn as before.

The first and second extracts are kept in separate vessels and covered with toluene to prevent bacterial action and, after being allowed to cool to room temperature, are neutralized with barium hydroxide to P_H 6.0. The bulk of the quinine remaining in solution separates as the sulfate and is filtered off. The first extract yields very little quinine sulfate, nearly all the base having been adsorbed by the fullers' earth, thus displacing the vitamin and kindred substances derived from the rice polish; subsequent extracts yield abundant amounts of quinine sulfate on neutralization, showing the presence of an excess of the reagent.

The quinine sulfate (mixed with barium sulfate) recovered from the first two extracts is returned to the tank with the fullers' earth to effect the third extraction. The volume of water is brought to about 70 liters when hot, otherwise the extraction is performed as before and the quinine is removed as in the previous cases.

The combined neutral extracts from 30 kilos of fullers' earth are tested by injection and are found to contain about 2,700,000 doses. Thirty kilos of fullers' earth correspond to 750 kilos of rice polish, originally containing about 3,000,000 doses, so that the recovery at this stage is about 90%. The foregoing operations have been carried out repeatedly on a large scale with consistent success, several tons of rice polish having been so processed in the past few years.

Barium Hydroxide Purification

Although the use of quinine sulfate for extraction purposes evidently possesses marked advantages, we were still unable to effect an isolation of crystalline material without the use of barium hydroxide as a subsequent means of purification of the quinine extract. If the above described quinine extract is made strongly alkaline with baryta, a copious precipitation occurs with very little loss of vitamin in the precipitate. Purification is best performed after the solution is concentrated 10-fold *in vacuo*. For this purpose the solution is first acidified with sulfuric acid to P_H 4.5 and the concentration is effected at a temperature not over 50°. In spite of this precaution we have experienced a substantial destruction of activity in concentration amounting to about 30% of the vitamin present. The cause of this destruction is uncertain and we have not yet discovered a satisfactory way to avoid it on a large scale. Omission of the concentration has been tried without improvement of final yield. This point requires further study. It seems probable that a further large economy of vitamin can be effected thereby.

Our practice has been after 10-fold concentration to

(4) R. R. Williams and W. H. Eddy, Carnegie Institution Year Book 1931–32, p. 321.

treat the extract with saturated barium hydroxide solution to P_H about 10. Exact adjustment is not feasible, expedition is necessary yet the proper amount of baryta is important. Enough should be used to remove nearly but not quite all the SO_4^- ion present. Proper adjustment of the amount of baryta produces a clear supernatant liquor on standing. Less baryta usually produces a turbid liquid. The solution is promptly clarified by centrifuging and the precipitate after one scanty washing is discarded.

The clear solution is now promptly brought to about P_H 9.0 with sulfuric acid and acidified by triturating it with a small excess of helianthin. The use of this reagent suggested itself in view of the fact that it forms sparingly soluble salts with a large number of nitrogenous bases.[5] However, its use requires discretion. If the solution is too alkaline appreciable amounts of vitamin are precipitated with the helianthates. If free barium is present, the precipitate formed upon addition of helianthin often assumes a gelatinous character as acidification proceeds and the final result is a stable gel comprising the entire solution. For these reasons we have found it wise to experiment with small trial quantities of each large lot of extract until the proper amounts of baryta and sulfuric acid are ascertained. The helianthates are best removed by filtration after standing overnight in a cold room. The filtrate and washings are now ready for precipitation with silver.

With proper adjustment the losses in baryta and helianthin operations combined may be kept below 5% of the vitamin present. These losses are determined by digesting the precipitates separately with dilute sulfuric acid. The filtrates from the barium sulfate and free helianthin respectively are injected in graduated doses after suitable adjustment of the P_H.

Subsequent Fractionation

The solution is acidified with sulfuric acid to P_H 2–3 and treated with silver nitrate in slight excess. Baryta is added to P_H 4.0. A relatively small precipitate of silver salts is filtered or centrifuged off and discarded. The P_H of the filtrate is now brought to 7.5 by adding baryta and the silver salt precipitate so formed is promptly collected and decomposed by triturating it repeatedly with an excess of dilute hydrochloric acid.

A minute aliquot of the filtrate and washings from the silver chloride is freed of traces of barium by cautious addition of dilute sulfuric acid and subjected to physiological test after it has been suitably diluted and neutralized. About 90% of the vitamin present in the filtrate from helianthates is recovered from the silver precipitate. The filtrate from the silver precipitate also contains a little vitamin as may be shown by injecting it after removal of silver as chloride and barium as sulfate. There is also perhaps a little loss in the process of decomposing the silver precipitate. The aggregate losses from all causes up to this point in the process are approximately 45% of the vitamin present in the original rice polish.

The solution resulting from decomposition of the silver precipitate contains total solids to the amount of 0.15 mg. per rat dose, indicating that the solids contain about 3% vitamin, assuming that 5 γ of the final crystals represents a dose. The volume of the solution is now greatly reduced so that the product from 100 to 200 kilos of rice polish can be handled conveniently in laboratory glassware of conventional sizes. It has been our practice to work on such a reduced scale from this point onward.

The P_H is adjusted to 3.0 by addition of baryta and the solution which may contain excess Ba but must be free of SO_4[6] is evaporated to a syrup *in vacuo*. The residue is treated with 15–20 cc. of hot 95% alcohol for each gram of solids present. A portion remains undissolved in the form of a gummy smear on the walls of the flask but if allowed to stand under the alcohol overnight this gum is converted into a white pulverulent and semi-crystalline mass which is readily dislodged and broken up by adding a few glass beads and rotating them about against the walls of the vessel. The insoluble deposit is removed by centrifuging, washed with a little 95% alcohol and discarded after a precautionary animal test. The clear alcoholic solution is again evaporated *in vacuo* to a thick gum which is treated as before with hot absolute alcohol in the proportion of 30 to 35 cc. per gram of solids. The second alcohol insoluble discard, very similar to the first in appearance, is more liable to contain appreciable amounts of vitamin. If tests indicate substantial losses this residue may be dissolved in a minimum of warm water, evaporated to a gum and redigested with strong alcohol.

The total solids in the alcoholic extract are now reduced to 0.075 mg. per dose, indicating a vitamin content of 6 to 7%. This extract is evaporated to dryness, the residue is dissolved in 5 times its own weight of water and benzoylated in the presence of an excess of sodium bicarbonate using benzoyl chloride equivalent to 1.5 times the weight of organic solids. The benzoylation step for which in its original form we are indebted to Seidell[7] is carried out at room temperature in a closed vessel from which air has been displaced by carbon dioxide. This precaution reduces the losses in this step to scarcely detectable proportions. Otherwise the losses may rise to 50% of the vitamin present. After the benzoylation reaction has subsided to negligible proportions, which may require ten to fifteen minutes, the alkaline solution is filtered with suction using a 2 to 3 millimeter layer of sodium bicarbonate on top of the paper to avoid clogging by gummy matters. The filtrate and washings are acidified with hydrochloric acid and filtered from benzoic acid which separates. The acid solution is allowed to stand overnight in the cold room and again filtered if necessary.

The clear filtrate is brought to P_H 5.0 with sodium hydroxide and excess 10% sodium phosphotungstate solution is added and the P_H brought to 1 to 2 with dilute sulfuric acid.[6] After testing to assure a slight excess of phosphotungstic acid, the solution is allowed to stand overnight in the cold and the precipitate is centrifuged off. The precipitate is suspended in dilute sulfuric acid and macerated for several hours. The precipitate is collected by centrifuge and decomposed by grinding five times with excess powdered baryta and small portions of water or till the washings are colorless. The combined extracts

(5) C. R. Stark and W. M. Dehn, THIS JOURNAL, **39**, 1378 (1917).

(6) W. K. Kinnersley, J. R. O'Brien and R. A. Peters, *Biochem. J.*, **27**, 232 (1933).

(7) A. Seidell, *J. Biol. Chem.*, **82**, 633 (1929).

are acidified with sulfuric acid to P_H 3.0 and sulfate is removed with barium chloride in slight excess. The solution now possesses activity in doses of 0.03 to 0.04 mg., indicating 12 to 15% vitamin content. The solution is evaporated *in vacuo* to dryness and allowed to stand overnight in the cold with 100 cc. of absolute alcohol per 50,000 doses of vitamin present. The material is now largely dissolved in the alcohol. A small white crystalline residue is removed by centrifugation and well washed with absolute alcohol.

The alcoholic solution and washings are evaporated to dryness *in vacuo*, dissolved in water and boiled *in vacuo* to remove the last of the alcohol. The aqueous solution is filtered from a slight insoluble residue and to the filtrate a 10% solution of gold chloride is added till no further immediate precipitation occurs. This requires about 5 times as much gold chloride as the weight of the vitamin hydrochloride present. After standing for one hour in the cold, the supernatant liquor is poured off the gummy gold precipitate which usually adheres to the walls of the vessel. The precipitate is rinsed with water containing a little gold chloride and is then promptly[8] decomposed by grinding repeatedly with water in the presence of an excess of molecular silver[9] till no further color is extracted. The black, loose mass of metallic gold, silver and silver chloride is separated by centrifuge and the solution is evaporated to dryness *in vacuo*. Often it is necessary to filter from traces of metals which deposit from colloidal solution in the course of evaporation.

The residue, usually a clear brown gum but often containing considerable amounts of crystalline vitamin hydrochloride, is dissolved in its own weight of water and to the solution are added about 20 volumes of hot absolute alcohol. On standing overnight the alcoholic solution deposits transparent, well-formed, blocky crystals of the vitamin hydrochloride. After standing for two or three days at room temperature the solution is decanted from the crystals which often adhere to the walls of the vessel. The crystals are rinsed with a little 95% alcohol, dried and weighed. The yield at this point is about 4 mg. per kilo of original rice polish. A further 1 or 2 mg. per kilo can be recovered from the mother liquor but not without difficulty. It is usually best to let the alcoholic mother liquor stand for at least five hours at about 0°. An amorphous flocculent deposit usually separates and is removed by centrifugation. The solution is now evaporated to dryness and the residue is dissolved in hot absolute alcohol. The alcoholic solution on account of the absence of water will deposit further amounts of amorphous material if allowed to stand at 0° for several days. This deposit is removed by centrifugation and the clear solution and washings are concentrated *in vacuo* to a small volume which on standing at room temperature usually deposits a second crop of crystals. The mother liquors are similarly reworked to secure a third small crop. The essential principle is the greater temperature coefficient of solubility of the amorphous material.

The order of use of reagents in the foregoing process is to a considerable extent determined by convenience, cost of chemicals, etc. A few points regarding order deserve special mention. The principal rejection of alcohol insolubles is best done before benzoylation; otherwise some of the alcohol insoluble substances appear to be converted to alcohol soluble forms and accompany the vitamin to the crystallization stage. Several times we have inserted a refractionation with phosphotungstic acid using P_H control as suggested by Kinnersley, O'Brien and Peters[6] but have not been uniformly successful. In one experiment, BCD in Table I, our yields of vitamin from the three phosphotungstate fractions: *viz.*, P_H 1–4, 4–5.5 and 5.5–7.0, respectively, were 161, 245 and 447 mg. In certain other instances our experience was consistent with that of Peters. Numerous other variants have been tried. Crystals in fair yield have been obtained by omission of the benzoylation step and of the gold step and even by the omission of both steps but there was some sacrifice in yield and cleanliness of the final crystals. The process above described is still undergoing refinement and promises substantially larger yields when more fully controlled.

The yields obtained from several lots of extract are shown in Table I.

TABLE I

YIELDS OF VITAMIN HYDROCHLORIDE

Experiment	Rice polish used, kilos	Yield of crystals, mg.	Yield per 100 kg. of polish, mg.	Remarks
1944	18.8	77	412	Phosphotungstic fraction P_H 4.0–5.5
2011	101.8	498[a]	489	All phosphotungstic fractions combined before gold pptn.
BCD	210	953[a]	454	Sum of all phosphotungstic fractions
E	70	294	420	Method detailed in text
F	70	239[b]		Method detailed in text
H	70	341	487	Method detailed in text
JKL	210	940	448	Method detailed in text

[a] Considerable contamination.

[b] First crop only. Remaining material scattered in attempt to expedite the process.

The crystals obtained as above described are not quite free of color nor of traces of flocculent matter. They melt at 246 or 247°. They are readily recrystallized from hot 95 to 97% alcohol and after one or two recrystallizations leave nothing to be desired from the standpoint of appearance. The melting point is now 249–250°. Detailed study of the purity and composition of recrystallized material will be reported at a later

(8) On standing for twenty-four to forty-eight hours substantial destruction has been observed with the separation of yellow flakes of metallic gold.

(9) H. W. Dudley, *Biochem. J.*, **23**, 1064 (1929).

time. Our present purpose is merely to indicate that the hydrochloride as obtained by us is essentially similar to that reported by others. The most significant criterion for this purpose is that of physiological activity. Representative curative tests on rats by the injection method appear in Table II.

TABLE II

CURATIVE TESTS ON POLYNEURITIC RATS

Prep. No.	Dose mg. × 10^{-3}	Result	Duration of cure, days
1920	3.75	Improved	..
	3.75	Recovered	10
	3.75	Improved	..
	5.0	Recovered	9
	5.0	Recovered	8
	5.0	Recovered	8
	7.5	Recovered	9
	10.0	Recovered	12
1944	3.75	Improved	..
	3.75	Recovered	5
	5.0	Improved	..
	5.0	Recovered	8
	5.0	Recovered	7
	7.5	Recovered	8

Additional evidence of a high level of curative effect was afforded by treatment of pigeons rendered polyneuritic by feeding on autoclaved wheat; 4 to 5 γ per os produced cures. Numerous feeding tests at various levels of dosage on both rats and pigeons will shortly be reported elsewhere. No polyneuritis has appeared in either case when the daily dose by mouth amounted to 0.005 mg.

This work has been aided for several years by generous grants from the Carnegie Corporation of New York through the Carnegie Institution of Washington. The authors wish to express their great appreciation for this aid.

Summary

A method is described for securing consistent yields of antineuritic vitamin hydrochloride of approximately 5 g. per ton of rice polish. This represents a recovery of about 25% of the amount present in the rice polish, a yield several fold larger than heretofore reported. The process has been developed on a factory scale up to about a thousand fold concentration of the vitamin. Thereafter the process is well handled in laboratory glassware.

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Synthetic Glycerides. V. Mixed Triglycerides of the Dilaurin Series[1]

BY O. E. MCELROY AND C. G. KING

The synthesis of mixed triglycerides has been undertaken primarily to provide compounds of known molecular structure analogous to the naturally occurring fats for the further study of their biological and physico-chemical relationships. Very little information is available concerning the chemical or physical properties of glycerides of known molecular structure, and much as recorded is erroneous, due to faulty methods of synthesis. The ease of migration of acyl groups from the β- to the α-position on glycerol has been responsible for many of the recorded errors.

Experimental

The acyl chlorides, used as intermediates, were prepared by the method recommended by McMaster and Ahmann,[2] from the acids (Eastman Kodak Co.) and thionyl chloride. The high molecular weight α-monoglycerides were prepared by the action of acyl chlorides on acetone-glycerol followed by hydrolytic removal of the acetone.[3] For the α-monoglycerides of acetic and butyric acids, the direct esterification method[4] was used. Fischer's method[5] for the preparation of symmetrical diglycerides was used in all cases, and followed by esterification with one mole of the second acyl chloride to furnish the symmetrical mixed triglycerides. The unsymmetrical isomers were prepared by treating the α-monoglycerides with two moles of the second acyl chloride.

Synthesis of Triglycerides

The preparation of the isomeric capryl dilaurins will serve to illustrate the general procedures followed.

α-Capryl-α',β-dilaurin.—Lauryl chloride (3.58 g.) dissolved in chloroform was added to a mixture of α-monocaprin (2.02 g.) and 4 g. of quinoline. The mixture was allowed to stand at room temperature for five days, taken

(1) This paper is based upon a dissertation presented by O. E. McElroy to the Graduate School in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) L. McMaster and F. E. Ahmann, THIS JOURNAL, **50**, 147 (1928).

(3) E. Fischer, M. Bergmann and K. Barwind, *Ber.*, **53**, 1589 (1920).

(4) H. A. Schuette and J. T. Hale, THIS JOURNAL, **52**, 1978 (1930).

(5) E. Fischer, *Ber.*, **53**, 1621 (1920).