

SUMMARY.

1. Acidotic, depleted, mature and young rachitic rats have been treated with alkaline saline mixtures of sodium, potassium and calcium to study the more beneficial mixtures for retention of all bases.

2. Most favorable results require all the bases, but the ratios are not without an important bearing.

3. Assuming that the K, Ca, P and Mg requirements are met, the alkalization requires a considerable preponderance of sodium, our best results in this survey resulting from a mixture in which Na:K = 5.9:1. This is simply a suggestive value, indicating the nature of the proper balance. A ratio of Na to K of 33 to 1, as in Experiment 1, showed some tendencies to imbalance.

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- (3) M. B. Richards, W. Godden and A. D. Husband, *Biochem. J.*, 21 (1927), 971.
- (4) F. W. Heyl and M. C. Hart, *JOUR. A. PH. A.*, 17 (1928), 225.

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PHYTOCHEMICAL NOTES.*†

No. 101. THE SEEDS OF *MONARDA PUNCTATA*.

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About two and three-quarter pounds of seeds were gathered at Lake Wisconsin and in the Pharmaceutical Garden. The heads were thrashed and the chaff removed with a fanning mill.

The moisture content, as determined by the xylene method¹ was found to be 3.6 p. c. (two determinations).

Ash content 2.6412 Gm. and 2.7580 Gm., respectively, when incinerated as directed² yielded the following amounts of

	I.	II.
Water soluble ash	0.0101 Gm. = 0.38 p. c.	0.0169 Gm. = 0.61 p. c.
Acid soluble ash	0.1816 Gm. = 6.87 p. c.	0.1836 Gm. = 6.66 p. c.
Acid insoluble ash	0.0081 Gm. = 0.3 p. c.	0.0076 Gm. = 0.2 p. c.
	0.1998 Gm. 7.55 p. c.	0.2081 Gm. 7.47 p. c.

Extraction with Selective Solvents.—One hundred Gm. of seeds were finely pulverized and placed in a continuous extractor for extraction with petroleum ether, ether and alcohol. The extraction with hot alcohol, acetone and methyl alcohol was accomplished in a flask connected with a reflux condenser. The

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† From the laboratory of Edward Kremers.

¹ U. S. Dept. Agr., *Circ.* 134.

² Nellie Wakeman, "Plant Chem. for Pharm. Students," page 15.

aqueous extractions were carried out in the usual manner. The amounts of extract resulting in each case are recorded. Duplicate experiments were carried out in each case.

Solvents.	I.	II.
Petroleum ether	27.7 Gm.	29.0 Gm.
Ether	0.3 Gm.	0.4 Gm.
Cold alcohol	2.2 Gm.	1.5 Gm.
Hot alcohol	0.7 Gm.	0.7 Gm.
Hot acetone	0.6 Gm.	0.4 Gm.
Hot methyl alcohol	0.5 Gm.	0.7 Gm.
Hot water	1.2 Gm.	1.5 Gm.
2 p. c. HCl solution	10.8 Gm.	10.0 Gm.
5 p. c. NaOH solution	29.0 Gm.	33.0 Gm.

The density of the combined petroleum ether extracts, as determined by means of a pycnometer, was found to be 0.9231; the refractive index (Zeiss) 1.4836 at 23°. S. V. 203.2 and 205.5, respectively. For the iodine value determinations 40 cc. of iodine solution were used in the first two determinations and 50 cc. in the remaining three. With one exception, concordant results were again obtained in this manner, *viz.*, 207.0, 207.8, 204.8, 207.3 and 208.2.

Extraction of Fixed Oil with Petroleum Ether.—The seeds were ground to a powder in a mortar, the meal packed in a reflux percolator and the fixed oil extracted with petroleum ether. Four samples of 163 Gm., 158.6 Gm., 149.3 Gm. and 150 Gm. of powdered seed yielded 33.5 Gm., 35.0 Gm., 33.8 Gm. and 37.8 Gm., respectively, of extract after removal of the hydrocarbon. These figures correspond to 20.5 p. c., 22.1 p. c., 22.6 p. c. and 25.2 p. c., respectively.

The saponification value of the oil was determined in the usual manner by heating for 1/2 hour with an excess of *N*/2 alcoholic potassium hydroxide and back titrating the excess with *N*/2 hydrochloric acid. The blank was run in the same manner. The saponification value was found to be 173.3.

The specific gravity of the oil at 25° C. was 0.9100, determined with a Mohr-Westphal Balance. As became apparent from experiments recorded below, this oil contained a small amount of petroleum ether.

After the petroleum ether had been recovered, the oil was subjected to steam distillation. About 5 cc. of a greenish yellow layer were obtained. This was separated from the water and exposed. All but a few drops evaporated. A Flueckiger test for thymol, gave a negative result.

The oil was saponified with alcoholic potassium hydroxide using twenty per cent in excess of the theoretical amount necessary. After refluxing for four hours the alcohol was recovered.

The soap having cooled sufficiently, the unsaponifiable portion was extracted by repeated shakings with ether. The soap was then acidified with 1:1 hydrochloric acid and the acidified solution drawn off and set aside for the identification of glycerin. The fatty acids were extracted with ether and the ether recovered.

Separation of the Solid from the Liquid Fatty Acids.—A concentrated solution of alcoholic potash was added until the solution was neutral to phenolphthalein. A 10-p. c. solution of lead acetate was added in excess and the mixture well stirred to insure complete formation of the lead soap. After the mixture was well

cooled, the supernatant liquid was filtered and the lead soap washed twice with hot water and finally with absolute alcohol. To insure complete removal of liquid, the soap was placed between filter papers. After the lead soap had been dried, it was placed in a larger beaker and twice the weight of ether added. The mixture was well stirred and the ether-soluble portion filtered into a separatory funnel. The insoluble portion was washed twice with ether. A 10-p. c. hydrochloric acid solution was added to the ethereal solution in the separatory funnel and the mixture shaken. The free fatty acids were thus dissolved in the ether layer and the precipitated lead chloride was removed. The solid portion was also placed in a separatory funnel with ether and 10-p. c. hydrochloric acid added and the precipitated lead chloride separated from the ethereal solution of the fatty acids by filtration.

Bromination of the Liquid Fatty Acids.—The modified method recommended by Lewkowitsch¹ was used. The ethereal solution of the free acids was placed in a two-liter Erlenmeyer flask and sufficient ether added to make the total about 800 cc., then 400 cc. of glacial acetic acid were added and the solution placed in an ice-bath.

After the solution had become well chilled, a solution of bromine in acetic acid, in the proportion of one part by weight of bromine to two parts of glacial acetic acid, was run in slowly through a separatory funnel agitating the solution well after each addition. A flocculent white precipitate began to be formed almost immediately. The addition of the bromine solution was continued until a slight reddish brown color had appeared and a faint odor of bromine was perceptible. The flask was then placed in a refrigerator for twenty hours.

The precipitate which had formed was filtered off and washed with equal parts of glacial acetic acid and ether. The white crystalline precipitate had a melting point of 180.5° C. The bromine content was found to be 60.73 p. c. and 60.34 p. c. (two samples). The melting point of stearic acid hexabromide is 181° C., and the bromine content is 63.27 p. c. while the tetrabromide derivative has a bromine content of 50.33 p. c. and m. p. of 113–114°.

The ether was recovered from the filtrate and the precipitate dissolved in petroleum ether. The petroleum ether solution was then placed in a refrigerator over night and the deposited crystals filtered off. They were recrystallized five times but the melting point remained at 95° C. The bromine content was found to be 46.25 p. c. and 45.95 p. c., respectively, on two samples.

The petroleum ether was recovered from the filtrate leaving behind a dark liquid. Ten Gm. of this residue were refluxed with 75 Gm. of granulated zinc with 200-cc. alcohol for 5 hours. The alcohol was partially recovered and the residue thrown into about 750 cc. of acidified water. The liberated fatty acids were neutralized with *N*/2 alcoholic KOH. The resultant soap was broken up with hydrochloric acid solution and the fatty acids shaken out with ether. After removal of the ether, a small amount of the residue was tested with 4 cc. of sulphuric acid and one drop of a 1 p. c. vanillin alcoholic solution and gave a violet ring (indication of oleic acid).² The I. V. was found to be 78.6 and 79.8 on two samples.

¹ "Chem. Tech. of Oils, Fats and Waxes," 1 (1921), 579.

² "Chem. Untersuch. ü. d. Früchte von *Cratægus Oxyacantha L.*," von L. Baechler, Colmar (1927), 47.

The lead soaps which were insoluble in ether were decomposed with acid in the presence of ether and the fatty acids obtained by removal of the ether. The residue was liquid indicating a very incomplete removal of the unsaturated acids. The fatty acids were taken up in a small amount of alcohol and placed in an ice-salt mixture. A few crystals came out of solution, however, not in sufficient amount to determine the melting point.

Extraction of Fatty Oil with Ether.—Four hundred and forty-six Gm. of seeds supplied by Prof. Richtmann were finely pulverized, sifted and repulverized in an iron mortar. The powder was then placed in a large Soxhlet extractor and exhausted with ether. After recovery of the ether, the extract was found to weigh 132.5 Gm. = 29.7 p. c. S. V. 206.0 and 207.8, respectively. Specific gravity determined with a pycnometer 0.9217 at 25° C. The refractive index (Zeiss) was 1.4840 at 23° C.

The U. S. P. method for the I. V. determination having given unsatisfactory results a larger amount of iodine was used; in the first experiment 40 cc. in place of 25 cc. and in the remaining determinations 50 cc. In this manner concordant results were obtained, *viz.* 207.0, 207.7, 207.4 and 207.3, respectively.

X-RAY CONTRAST MEDIA.*

BY BERNARD FANTUS, M.S., M.D.

The miracle of looking into the interior of the body, of examining and photographing almost each and every one of its major structures has been accomplished by reason of the selective absorption of the Roentgen rays by various tissues of the body; and, where this is insufficient, the introduction of contrast media. These latter are of interest to the pharmacist, as he may be called upon to prepare and supply a number of these.

The great difference in the absorptive power of various materials can best be comprehended by an understanding of the law, that *the absorption of X-rays by media is approximately proportional to the fourth power of the atom number of position of the element in the periodic system.* Table I may serve as a basis for the illustration of the truth of this "law."

TABLE I.—ATOM NUMBERS OF ELEMENTS OF PRACTICAL IMPORTANCE.

Hydrogen.....	1	Chlorine.....	17
Carbon.....	6	Bromine.....	35
Nitrogen.....	7	Iodine.....	53
Oxygen.....	8	Barium.....	56
Phosphorus.....	15	Lead.....	82
Calcium.....	20	Bismuth.....	83

Hence an atom of calcium with its atom number of 20, absorbs about 40 times more X-rays than an atom of oxygen with its atom number of 8 for:

$$20^4 : 8^4 :: 160,000 : 4,096, \text{ equals approximately } 40.$$

From this it will be seen that the absorptive power increases enormously as we proceed down the scale.

* October meeting of Chicago Branch, A. Ph. A.