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SOME CONSTITUENTS OF JAMBUL.

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The Jambul Tree (*Syzygium Jambolana*), well known to the natives of the East Indies and Malay regions from China to New South Wales, for its edible fruit, is a large tree belonging to the *Myrtaceae*, sometimes attaining the height of ninety feet. A careful gleaner of the medical literature finds that three parts, the seed, pericarp and bark, have been employed in the treatment of *diabetes mellitus* with questionable results, but is perhaps impressed by some beneficient results reported. Two parts of the plant, the bark and the pericarp, have been recognized in the pharmacopeia of the Netherlands.[1]

The berry-like, sour fruit is about as large as the olive, and apparently forms a readily procurable commodity in the European market, whereas the term Jambul as used in this country refers to the flinty. hard seed contained in the pericarp. There is also some difference in opinion as to the part of the plant which should be employed in the manufacture of the fluid extract.

The early chemical studies showed the presence, in the bark, of tannin,[2] in the seed, of gallic acid.[3] The seed yields a trace of ethereal oil, 0.37% fat, and 0.3% resin, and pharmaceutical shrewdness, rather than chemical investigation, or conformance with a rational system of nomenclature, has given the name "antimellin" to an alleged glucosidic constituent.[4] This finding of Börsch could not be substantiated by Power and Callan.[5] The statement of Pottiez[6] concerning the presence of quercitol and cinnamic acid could not be confirmed by these chemists. Stephenson[7] found that the diastatic hydrolysis of starch was appreciably reduced by the presence of the extract of the fresh kernels.

Several preparations of German origin are marketed, *e. g.*, Djoeat, Bauers, Glykosolvol and Pavykol, which probably contain, in part, extracts from the bark or pericarps, and Djoeatin (Börsch) which is alleged to contain the above-mentioned "antimellin." The presence of tannin has recommended its use among the natives as an astringent, but on the whole, as stated in the Dispensatory, "it has failed to establish itself as a practical medicament."

The recent work of Power and Callan on Jambul seed, leaves the ques-

[1] *Ph. Nederl*, IV.

[2] Johanson, Dissert., Dorpat, 1891.

[3] Elborne, *Pharm. J.*, 3, 932 (1888).

[4] Börsch, *Pharm. Ztg.*, 44, 574 (1899).

[5] *Pharm. J.*, 34, 414 (1912); 91, 245 (1913).

[6] *Ann. Pharm. Louvain*, 5, 373, 490 (1899).

[7] *Pharm. J.*, p. 211 (1892).

tion as to the pharmaceutical value of the pericarp. It was our plan to make a comparative study of the seed and pericarp, and we decided to investigate independently the seed, while awaiting a promised supply of pericarp, which unfortunately will not be available at present and we therefore report our work on the seed.

Our sample of Jambul seed, which was badly worm eaten, was received from Bombay. It was picked over and 91 pounds were rejected from a 200-pound shipment. The material contained 8.0% moisture and 2.9% ash. Ligroin extracted 1.2%, ether 1.3%, and alcohol 16.1%. The residue insoluble in alcohol had the following composition: crude fiber, 2.3%; pentosans, 2.1%; protein, 6.3%; starch, 41.4%; dextrin, 2.1%. The alcohol extract showed the presence of 0.3% sucrose and 3.3% reducing sugars. Tannin amounted to 6.0%.

The products present in the alcoholic percolate, and soluble in water, besides the sugars and tannin, are ellagic and gallic acids.

The study of the resin gave, in general, the same results as those reported by Power and Callan, *i. e.*, from the ligroin extract, oleic, linoleic, palmitic and stearic acids; from the ethyl acetate and alcoholic extracts, chiefly ellagic acid. We are, however, able to describe more fully the presence in the ligroin extract of myricyl alcohol, of a hydrocarbon very probably hentriacontane, and of a phytosterol, $C_{27}H_{46}O$, melting at 135–135.5° that formed an acetate, melting at 119–120°. The ether extract as well as the chloroform extract yielded in addition a phytosterolin, $C_{33}H_{56}O_6$, which we have described in detail.

We endeavored to repeat Stephenson's work which would indicate the presence of something in Jambul that would retard diastatic hydrolysis. In using the iodine method of Sherman, Kendall and Clark,[1] it was found to be impossible to read the end points of a diastatic hydrolysis because the presence of gallic acid in the extract decolorized the iodine solution. In the same way the reducing action of a Jambul extract is sufficiently great to render inaccurate their excellent gravimetric method employed for finding the activity of pancreatin.

Experimental.

(*A*) **Proximate Analysis.**—A sample of the air-dried seed after grinding and sieving was quantitatively extracted with various solvents, with the following results:

Extract.	Per cent.
Ligroin (35–55°)	1.2
Volatile ether extract	0.2
Ether	1.3
Alcoholic	16.1

The proximate analyses were conducted in accordance with the usual methods, and gave the result tabulated below:

[1] THIS JOURNAL, 32, 1073 (1910).

	Per cent.		Per cent.
Moisture	8.0	Protein	6.3
Starch (diastase)	41.4, 40.3	Ash	2.9
Crude fiber	2.3	Dextrin	2.1
Pentosans	2.1	Tannin[1]	6.0

The quantitative examination of the alcohol-soluble carbohydrates resulted as follows:

100 g. of Jambul seeds were extracted with boiling 95% alcohol. The alcoholic extract was concentrated to a syrup, precipitated with a slight excess of lead subacetate and made to a volume of 200 cc. The direct and invert readings at 22° in 2 dcm. tube are —2.6V, and 3.2V, respectively. The invert reading at 86° in a 2 dcm. tube was 0.35V. Hence sucrose = 0.23%, fructose = 2.3%, and glucose = 2.1%, respectively. Gravimetric determinations by the Walker-Munson process gave sucrose 0.33% and reducing sugar 3.3%.

(*B*) **Examination of Alcoholic Extract.**—For this purpose 45.4 kg. were exhausted by percolation with wood alcohol at room temperatures. Power and Callan extracted the seed with hot ethyl alcohol. The percolate (397 l.) was concentrated under diminished pressure to a volume of 12.5 liters. This concentrated extract on standing deposited 230 g. of yellowish material which was quite insoluble in the usual organic solvents. It could be redissolved in dilute alkali and then reprecipitated by the addition of acetic acid. After being digested with ether, and with ethyl acetate, this material was crystallized from pyridine. Brown needles were obtained that gave the characteristic tests for ellagic acid.

The filtered alcoholic extract was poured into 25 l. of distilled water and vigorously agitated. After long standing the resin was removed by filtration. The aqueous alcoholic filtrate was concentrated under reduced pressure in order to remove the alcohol. When this solution was diluted with distilled water, further precipitation took place even after diluting to a volume of 80 liters. The solution was allowed to stand overnight and the precipitate (372 g.) was filtered off. This material was of the nature of a phlobaphene. The filtrate was concentrated to a volume of 9.77 l. It now deposited 84 g. of ellagic acid. This deposit was digested with ether and with ethyl acetate and crystallized three times from pyridine. The crystals were washed successively with water, ethyl acetate and ether, dried at 150° and analyzed.

Calc. for $C_{14}H_6O_8$: C, 55.6; H, 2.0 Found: C, 55.6; H, 2.1.

The aqueous solution containing 5276 g. of water-soluble plant extractive was divided and a quantity containing 3750 g. was extracted repeatedly with large volumes of ether, which extracted 524 g. of a greenish white solid, which proved to be gallic acid. This amounts to 1.63% of the drug. A portion of this crude gallic acid was digested with fresh ether, which removed the color. The residue crystallized from water in colorless

[1] Both the Hide powder method, and the Proctor-Lowenthal method gave the same results.

needles, decomposing at about 240°. It was dried at 115° and identified as gallic acid:

Calc. for $C_7H_6O_5$: C, 49.4; H, 3.5. Found: C, 49.4; H, 3.4.

The dark green ethereal filtrate from the purified gallic acid was exhaustively examined, and a small quantity of sulfur melting at 114–115° was identified as a constituent.

The aqueous solution which had been completely extracted with ether, was now extracted with chloroform, which extracted only 3 g. of material. This was redissolved in chloroform and fractionally extracted with the usual alkaline solvents which yielded nothing definite. The neutral solution upon evaporation yielded a minute quantity of crystalline material melting at 115–121°. This gave the color tests of the phytosterol group.

The aqueous solution which had been completely extracted with ether and chloroform was now extracted repeatedly with hot amyl alcohol. During this extraction there ensued a gradual precipitation of ellagic acid. The material extracted with amyl alcohol weighed 742 g., equivalent to 2.2% of the drug. This extract contains a considerable quantity of ellagic acid. The amyl alcoholic extract could be prepared as a greyish white powder, by precipitation with petrolic ether. From dilute alcohol and from pyridine solutions, ellagic acid separated. A part (58 g.) of the amyl alcoholic extract was redissolved in this solvent and the solution was extracted with the usual alkaline solvents, but nothing crystalline was separated by this procedure. Another part (127 g.) was hydrolyzed by boiling for several hours in the presence of 5% sulfuric acid, but no crystalline hydrolytic products were found. Eighty-four grams were hydrolyzed by boiling for one minute with 10% potassium hydroxide solution. The mixture was cooled and poured into an excess of dilute sulfuric acid, and then steam distilled. From the contents of the flask a quantity of gallic acid, melting at 240–242°, was isolated.

A quantity (171 g.) was boiled with a large volume of water and then vigorously steam distilled. Ellagic acid separated. The solution was concentrated and further quantities of ellagic acid separated. At length, after evaporation to dryness, the residue was boiled with ethyl acetate and some insoluble material (ellagic acid) was removed by filtration. It was impossible to obtain crystals from this solution. The ethyl acetate solution was evaporated to dryness, and again taken up in dry ethyl acetate, in which it was freely soluble, but nothing definite could be obtained from it. The amyl alcoholic extract is not glucosidic.

The aqueous liquid which had been extracted with ether, chloroform, and with amyl alcohol, was freed from the latter immiscible solvent by a vigorous steam distillation. The distribution of nitrogen in this solution was as follows: Total soluble nitrogen, 0.0649%; ammonia nitrogen, 0.0079%; lead subacetate precipitable nitrogen, 0.0197%.

In order to test for acid amides, one-fifth of the solution was precipitated with mercuric acetate solution, but the results were negative.

The remainder of the solution was precipitated with basic lead acetate, filtered, and the precipitate was found to consist essentially of lead tannate.

The filtrate from the lead tannate was freed from lead with hydrogen sulfide and sharply concentrated. Although this syrup yields a precipitate with phosphotungstic acid, no nitrogenous bases were isolated from this fraction. The only product found was sugar, a crystalline deposit of a *d*-phenylglucosazone melting at 207–208° being readily prepared. Pentose sugars were absent.

The Examination of the Resin.—The resin which precipitated when the alcoholic extract was poured into water weighed about 699 g., equivalent to 1.5% of the drug. It was dissolved in wood alcohol, poured upon purified sawdust, transferred to a continuous extractor, and extracted with the following results:

Ligroin (40–60°)	433 g.
Ether	20
Chloroform	13
Ethyl acetate	79
Alcohol	109
Total,	654 g.

The Ligroin Extract.—Three hundred grams were dissolved in ether and shaken with solutions of potassium hydroxide (5% and 10%). The alkaline extractions were acidified and extracted with ether. This ethereal solution was successfully extracted with a solution of ammonium carbonate (10%) but these extracts yielded nothing but a small quantity of smeary material precipitable with acid.

The ethereal solution was now extracted with solutions of potassium carbonate, and the fatty acids occurring free in the plant were removed. The alkaline extract containing the potassium salts of these fatty acids was acidified and extracted with ether. The ethereal solution of fatty acids was dried over anhydrous sodium sulfate. The ether was removed and a residue of about 92 g. obtained. This was distilled under diminished pressure. The boiling point was 215–250° at 20 mm., and the iodine number of the distilled acids which solidified in the receiving tube was found to be 88.7. A very considerable quantity of this material could not be distilled and it remained as a tar in the flask. These fatty acids were studied in connection with those obtained upon the subsequent hydrolysis of the glycerides.

The ether solution which had been extracted with ammonium carbonate and potassium carbonate was now extracted with a solution of potassium hydroxide. The alkaline extract was acidified and a quantity

of tarry material (15 g.) precipitated. This was dissolved in alcohol and subjected to acid and alkaline hydrolysis, but nothing crystalline could be separated in either case.

The ether solution which had been extracted with solutions of ammonium carbonate, potassium carbonate and potassium hydroxide contained 17 g. of neutral material belonging to the unsaponifiable material. It boiled at 120–250° at 15 mm., and yielded oily distillates exactly corresponding to those described among the unsaponifiable products of the fat.

The original ethereal solution of the fat which had been extracted with solutions of potassium hydroxide was evaporated to dryness and the residue was saponified by boiling with 250 cc. of 10% alcoholic potash for about five hours. The alcohol was removed and water added to completely precipitate the unsaponifiable material, which was extracted with ether.

Examination of the Unsaponifiable Matter.—The dried solution was evaporated to dryness and the residue was an orange-colored oil amounting to 47 g. It was dissolved in absolute alcohol and upon standing 0.15 g. of material separated. The melting point was indefinite (62–76°) and suggested, as stated by Power and Callan, a mixture of hydrocarbon and a higher alcohol. By means of the phthalic acid fusion, and subsequent extraction with sodium carbonate, a small quantity of a hydrocarbon melting at 61° was isolated. Three crystallizations from ethyl acetate raised this melting point to 63°. It separated in colorless leaflets and was perhaps impure hentriacontane.

Calc. for $C_{31}H_{64}$: C, 85.3; H, 14.7. Found: C, 85.1; H, 14.1.

A small quantity of a sodium salt of an acid phthalic ester was isolated and boiled with alcoholic potash. A product separated which had the melting point of myricyl alcohol, 82–84°. It crystallized from alcohol in leaflets, which softened at 82° and melted at 85°.

Calc. for $C_{30}H_{62}O$: C, 82.2; H, 14.1. Found: C, 81.7; H, 13.5.

The alcoholic solution from which the hydrocarbon and myricyl alcohol had separated yielded no further crystallizations even from concentrated solutions after the addition of small quantities of water. This residue was distilled under diminished pressure.

Fraction I (b. p. 120–160° at 10 mm.). This was a colorless, limpid oil with a fragrant odor. The weight was 11 g.

Fraction II (b. p. 160–200° at 10 mm.). This was a colorless oil, less mobile than the first fraction, and of about the same weight. A systematic fractional distillation of I and II effected no separations.

Fraction III (b. p. 200–250° at 10 mm.). This was a thick viscid oil which partially solidified. It weighed about 5 g.

The fractions collected above 250° at 10 mm. solidified in the receiver. The fraction boiling at 280–340° at 10 mm. was crystallized from ethyl

acetate. The material melted at about 132°, but softened somewhat lower. It was necessary to separate a small quantity of low-melting material (70–75°) by a fractional crystallization and phytosterol then separated in glistening plates, melting sharply at 135–135.5°.

Calc. for $C_{27}H_{46}O.H_2O$: H_2O, 4.5. Found: 5.6%.
Calc. for $C_{27}H_{46}O$: C, 83.9; H, 11.9. Found: C, 83.8; H, 11.6.

0.1163 g. of the anhydrous phytosterol made up to 20 cc. with chloroform showed a rotation of —0.489 in a 2 dcm. tube, whence $[\alpha]_D^{25} = -42.04°$.

It yielded an acetyl derivative that separated from acetic anhydride in thin plates which melted at 119–120°.

Examination of the Fatty Acids.—The alkaline solution from which the unsaponifiable matter had been extracted with ether was acidified and the liberated fatty acids were extracted with ether. The ether solution was dried over anhydrous sodium sulfate, concentrated to a small volume and and then largely diluted with ligroin which precipitated some tarry material. This was removed by filtration, and the solvent was distilled from the fatty acids. These boiled chiefly at 230–260° at 15–20 mm. A small fraction distilled at 260–280° at 20 mm. The weight of distilled acids was 30.1 g., and the iodine number was 98.3.

These acids were mixed with those which had been extracted with potassium carbonate solution. A portion weighing 22.5 g. was converted into the lead salts, which were treated with ether. The liquid acids obtained from the lead salts soluble in ether weighed 12.9 g. (57.3%). These boiled chiefly at 235–245° at 32–34 mm.

Calc. for $C_{18}H_{34}O_2$: C, 76.6; H, 12.1; iodine no., 90.1; for $C_{18}H_{32}O_2$: C, 77.1; H, 11.4; iodine no., 181.4. Found: C, 76.6; 76.7; H, 11.3, 11.55; iodine no., 131.7.

The liquid acids therefore consist of a mixture of oleic and linoleic acids.

The lead salts of the fatty acids, insoluble in ether, were decomposed with hydrochloric acid and the solid fatty acids separated in the usual manner. When dissolved in absolute alcohol with the object of separating any of the more insoluble acids by crystallization, it was found that the acids were very readily soluble and no satisfactory crystallization could be obtained even from very concentrated solutions. The alcoholic solution was fractionally precipitated with an alcoholic solution of barium acetate. This yielded Fractions I and II. Fraction III was precipitated by the addition of water.

I. Melting at 51–53°. C, 75.8; H, 12.4; N. v., 204.3.

III. This fraction was an oil and gave entirely anomalous analytical data. Iodine no., 35.2, 34.7; neutralization value, 34.9; and saponification value, 140.2.

The solid acids are therefore a mixture of palmitic and stearic acids.

Calc. for $C_{16}H_{32}O_2$: C, 75.0; H, 12.5; N. v., 219.1. $C_{16}H_{30}O_2$: C, 76.1; H, 12.7; N. v., 197.5.

The Ether Extract of the Resin, which amounted to 20 g., contained a quantity (2 g.) of an insoluble white solid. This was filtered off. When this substance was dissolved in chloroform, in the presence of a few drops of acetic anhydride, and sulfuric acid was added, a play of colors resulted showing at first transient pink, then blue, and finally a beautiful green. It was crystallized several times from dilute pyridine, and then melted at 275–285°. It was a phytosterolin. After being dried to constant weight at 120° it was analyzed.

Calc. for $C_{33}H_{56}O_6$: C, 72.3; H, 10.2. Found: C, 72.3; H, 10.2.

A portion of this was converted into an acetate, which crystallized from dilute alcohol in colorless, glistening leaflets melting at 167–168°.

0.5036 g. of the anhydrous phytosterolin acetate, when made up to 20 cc. with chloroform, showed a rotation of —1.21° in a 2 dcm. tube, whence $[\alpha]_D^{23} = -24.1$.

One gram of this phytosterolin was hydrolyzed according to the method outlined by Power and Salway.[1] It was dissolved in 60 cc. of hot amyl alcohol and 20 cc. of an aqueous 15% solution of hydrochloric acid added, together with sufficient ethyl alcohol to form a homogeneous liquid. After heating for three hours in a reflux apparatus, steam was passed through the mixture to remove the amyl alcohol, and the contents of the flask then filtered. A solid substance was thus collected, which after several crystallizations from ethyl acetate, alcohol, and dilute alcohol, separated in glistening leaflets melting at 134–135°. The mother liquors from this crystallization contained a relatively large quantity of an oily resinous material which had evidently been formed from the phytosterolin by too prolonged hydrolysis. The crystals gave the phytosterol color reaction.

0.0983 g. made up to 20 cc. with chloroform had a rotation of 0.38° in a 2 dcm. tube, whence $[\alpha]_D^{25} = -38.8$.

Calc. for $C_{27}H_{46}O$: C, 83.9; H, 11.9. Found: C, 83.3; H, 11.3.

The acid aqueous liquid, from which the phytosterol had been separated by filtration, was exactly neutralized with sodium carbonate, evaporated to dryness, the residue digested with absolute alcohol, and the mixture filtered. On evaporating the alcoholic filtrate a small amount of syrupy residue was obtained, which reduced Fehling's solution, and yielded an osazone melting and decomposing at 212°. It was thus evident that the sugar was glucose.

Thus this phytosterolin is shown to be phytosterol-*d*-glucoside.

The ether extract from which the phytosterolin had been separated was fractionally extracted with varying strengths of alkali. The potas-

[1] *J. Chem. Soc.*, 103, 399 (1913).

sium hydroxide extracts removed practically all the dissolved matter as a green oil which after some time became semi-solid. This could not be crystallized and was unchanged when boiled for several hours in the presence of an alcoholic solution of 5% sulfuric acid solution.

The Chloroform Extract of the Resin weighed 13 g. Part of this extract was quite insoluble in ethyl acetate and alcohol with which it was digested. This part was crystallized twice from dilute pyridine and melted at 280–295°. This gave the usual color test for a phytosterolin. After crystallization it weighed 3 g. Altogether the phytosterolin isolated from the ether and chloroform extracts amounted to 5 g. or 0.011% of the air-dried drug.

The filtrate from the above phytosterolin was evaporated to dryness, taken up in chloroform, and then fractionally extracted with varying strengths of alkali. Nothing of a crystalline nature was obtained by this procedure.

The Ethyl Acetate Extract of the Resin was a mixture of ellagic acid and tannin-like substances. Upon distilling off a portion of the ethyl acetate about half of it separated as crude ellagic acid, which when crystallized once from alcohol yielded 13 g. of pure acid that did not melt at 350°. The mother liquor from this separation was a smear, that colored ferric chloride solution black, and precipitated a gelatin solution.

The part soluble in ethyl acetate was thoroughly examined but nothing was isolated.

The Alcoholic Extract of the Resin yielded 15 g. further of ellagic acid. The total ellagic acid separated amounts to 1.2% of the plant. Neither an acid hydrolysis or a potash fusion gave any interesting decomposition products. Neither the ethyl acetate fraction nor the alcoholic extract was glucosidic.

KALAMAZOO, MICH.

NEW BOOKS.

Laboratory Manual of Inorganic Chemistry for Colleges. By LYMAN C. NEWELL, Ph.D., Professor of Chemistry, Boston University. Boston: D. C. Heath & Co. Pp. vi + 240.

Although this book is prepared primarily to be used as a laboratory guide in connection with the author's "Inorganic Chemistry for Colleges," the experiments are of such a nature and scope that it could be used advantageously with any standard text. The directions for the experiments are clear and definite, and are based on the author's long experience as a laboratory teacher. A large number of experiments of graded difficulty are given, and provision is thus made for students of widely different preparation in chemistry. The apparatus required for most of the work is simple and inexpensive. The book appears to be one that