COOH	COOH
•	•
HCOH	OHCH
•	•
C_6H_5	C_6H_5
Dextro-mandelic acid,	Levo-mandelic acid,
$[\alpha]_D^{20} = +153$.	$[\alpha]_D^{20} = -153$.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE SHEFFIELD LABORATORY OF PHYSIOLOGICAL CHEMISTRY, YALE UNIVERSITY.]

THE EDIBLE LITCHI NUT (Litchi Chinensis).

BY B. E. READ.

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The so-called Chinese hazel nut, *Litchi Chinensis* Sonner, (syn. *Nephelium litchi, Litchi* Sonn.), together with the allied species of the *Nephelium* occurs in the tropical countries of the far east where it is cultivated for medicinal and edible purposes. The litchi belongs to the genus *Alectryon* of the natural order *Sapindaceae*, which genus consists of more than 16 species, all of which are arborescent and are distributed over the Malayan, Papuan and Pacific Islands, being represented in the latter 2 groups by this particular species *Nephelium*. The type of this genus is the Titaki of New Zealand, *Alectryon excelsus*, which like the Hawaiian Mahoe has edible fruits.[1] It is singular that while the leaves and branches of many of these trees are unquestionably poisonous the fruit of others is valuable as an article of diet. The litchi nut and the longan and rambutan fruits as such are greatly appreciated for their excellent flavor and are used in "inflammatory and bilious fevers."

Of these many useful fruits only one, the litchi nut, has established itself through Chinese sources on the American market. There are said to be 8 varieties of this nut, which may account for varying reports about them. Those imported here from Canton are nearly globose with a dull brick-red pericarp which when ruptured exposes a sweet, brown, fleshy arillus surrounding a glossy chestnut-brown, orbicular seed, described in detail by Engler and Prantl.[2]

The litchi nut has long been used by the Chinese in medicine, the following paragraph from the Chinese Materia Medica giving a good idea of how highly it is esteemed by them.[3]

Nephelium Litchi.—Many of the sapindaceous plants are poisonous but the nephelium fruits are an exception, being much esteemed both in the fresh and dry

[1] J. F. Rock, "The Indigenous Trees of the Hawaiian Islands" (1913).

[2] Engler und Prantl, "Die Natürlichen Pflanzen-familien," Wilhelm Engelmann, Leipzig (1896).

[3] Stuart, G., "Chinese Materia Medica." Published by *Presbyterian Mission* Press, Shanghai (1911).

state. Fukien Litchi is regarded as the best. The fruits are dried in the sun or by artificial heat, and are used as sweetmeat at feasts, and often given as presents to the newly married. They are not regarded as entirely without deleterious properties, and when the raw fruits are partaken of freely they are said to produce feverishness and nosebleed. Partaken of in small quantity or in the dried form they are thirst relieving and beneficial to nutrition. But they are specially recommended in all forms of gland enlargements and tumors. The seeds are regarded as anodyne and are prescribed in various neuralgic disorders and in orchitis. The leathery external tegument of the fruits is used in decoction in the distress caused by small-pox eruption, and also in fluxes from the bowels. The flowers, bark and root are employed in decoction in angina and quinsy.

It is furthermore cited by Hooker in "The Flora of British India," and by Kurz in "The Forest Flora of British Burma," the variety mentioned having a white edible arillus. In the latter country it is specially cultivated at Chittagong and has a local name "Kyet Mouk," though probably not indigenous there.

In view of the above facts and the present efforts toward food economy it was thought profitable to investigate the composition of these nuts, to obtain a correct estimate of their food value and moreover to look for the reason of their popularity as a drug in curing sickness.

Therapeutic Activity.—The diseases mentioned suggest the possible presence of iodides, alkaloids or a bitter substance of strong therapeutic action. The mention of feverishness and nosebleed produced when the nuts are freely partaken of, together with the fact that this plant is a member of the soapwort family would point to the presence of a saponin. No iodine was found present to account for its alleged action on tumors and gland enlargements, such as present-day treatment for goitre would suggest, and no saponin or similarly active substance was detected to account for its supposed toxicity. When added to the regular diet of a rabbit, for a long period or when fed in as large a quantity as 50 g. at one time, no toxic effects whatever from the nuts were observed.

These results confirm the opinion that statements regarding old native drugs may be very inexact and unreliable; which is not surprising when one remembers the empirical development of old Chinese medicine, its confused ideas about disease, and its lack of specific scientific facts concerning the name, natural order and habitat of any plant used.

Food Value.—The proximate composition of the litchi has been estimated by Atwater and Bryant.[1] Like the chestnut it is practically fat free, contains little, if any, protein, and consists very largely of "fiber and nitrogen free extract." The latter was found to be composed almost entirely of simple sugars, which accounts for the inclusion of these nuts as a food and for the claim that they are "beneficial to nutrition."

The various extracts prepared were acid, and showed the presence of

[1] U. S. Dept. Agr. Off. Exp. Sta., *Bull.* 28.

citric acid with possible traces of the other common fruit acids, which stimulate the appetite and are well known as "thirst relieving substances." There was no pectin body present; but this fruit with its high sugar and acid content on the addition of orange fruit would form an excellent jelly suitable for nephritic and other limited diets, required for diminishing the acidity of the urine.[1]

It is reported by Street[2] that owing to its high carbohydrate content 7 g. of litchi are of equivalent calorific value to 10 g. of wheat bread. No other of the many fresh fruits or nuts cited by him show as high a value. I have found the carbohydrate to be a mixture of simple sugars chiefly invert sugar, a carbohydrate easily digested with all its energy available for use in the body.

Examination of the ash showed considerable content of the mineral salts needed in a well-balanced diet; thus the nut would make a good supplement to foods rich in protein and those lacking in mineral matter.

The many valuable suggestions of Langworthy[3] on the use of fruit as a food could be applied to the canning, preserving, drying, and general preparation of this fruit as a wholesome, palatable and attractive addition to the diet.

Experimental Part.

The proximate analysis corresponded with that given by Atwater and Bryant[4] as follows:

Ash, 1.5%; protein, 2.9%; ether extract, 0.2%; fiber and nitrogen-free extract, 77.5%; water, 17.9%.

I obtained very different values for the last 2 items; the amount of water might easily vary in a dried preparation like this.

2.1809 g. heated at 105° to constant weight lost 0.889 g. = 40.8%.

Preliminary Examination.—A preliminary qualitative examination was made of a simple aqueous extract prepared by rubbing up the fruit with water. The solution obtained had a strong reducing action on Fehling's solution, was levorotatory, fermented readily with yeast, yielded a small amount of a hydrazone when treated with phenylhydrazine in the cold for 24 hours. When heated with the same reagent for 10 minutes on the boiling water bath it formed a large amount of an osazone melting at 203°. A strong reaction was obtained with Seliwanoff's test for levulose. Biuret and various other protein tests gave negative results with the water extract. Hot water extracts showed no visible reaction with iodine or iron salts, indicating the absence of starch or tannin.

Five fruits weighing approximately 13 g. were thoroughly extracted with

[1] Editorial, *J. Am. Med. Assoc.*, **69**, 1433 (1917).

[2] Street, J. P., "Diabetic Foods," *Conn. Agr. Exp. Sta.*, p. 93 (1913).

[3] U. S. Dept. Agr., *Farmer's Bull.* **293** (1917).

[4] *Loc. cit.*

cold water. The clear solution obtained after filtering off a small amount of insoluble fiber was diluted to 1000 cc. and the rotatory and reducing power estimated. There was no increase in either value after hydrolysis of the solution with acid, thus showing the absence of complex sugars.

25 cc. of the solution gave by Allihn's method 0.3834 g. CuO. For pure invert sugar this is equivalent to 664 mg. per 100 cc., or 51.1% of the original substance.

The solution placed in a 2 dcm. tube gave a rotation of —0.95 V°. This reading is a little too high for 51% of invert sugar and indicates the presence of traces of other levorotatory substances.

A detailed scheme of analysis was made based chiefly on that outlined by Street and Bailey.[1] Successive alcoholic, aqueous, acid and alkaline extracts were prepared for examination of their carbohydrate content and estimation by Allihn's copper method. Other less significant data were obtained relating to acid content, crude fiber, etc.

Alcoholic Extract.— 100 g. of the edible portion were finely divided and heated with 1000 cc. of 95% alcohol on a boiling water bath for 8 hours. Nearly all of the fruit dissolved. After standing 24 hours, the small insoluble portion, weighing 8.0 g. when dried, was filtered off.

The alcoholic extract was evaporated nearly to dryness on a boiling water bath, and taken up in 1000 cc. of water. The solution obtained was treated with lead acetate in the usual way, and the clear filtrate after dilution with 7 volumes of water used to determine reduction and polarization values. The values obtained corresponded with those of the preliminary aqueous extract; hydrolysis with acid also made no change.

Portions of 25 cc. of the solution yielded 0.3784 g. CuO. This is approximately the amount of CuO obtainable if all the soluble material were invert sugar. It is equivalent to 52.9% invert sugar.

Aqueous Extract.—The dried residue from the alcoholic extraction was further extracted with 400 cc. of cold water for 48 hours. The dark-colored solution obtained was filtered off and treated with lead acetate which cleared and almost decolorized it. The solution showed no rotation or reduction of copper solution, the sugars having all been withdrawn in the alcoholic extract.

Acid Extract.—The residue was treated with 250 cc. of 1% hydrochloric acid for 6 hours on a boiling water bath to extract the hemicelluloses. Aliquot parts equivalent to 20 g. of litchi yielded 0.045 g. CuO by Allihn's method. This is equivalent to 0.1% glucose-yielding substance in the original fruit.

Alkali Extract.—The small amount of remaining insoluble material was boiled with 200 cc. of 1% caustic soda for 45 minutes and filtered. The extract when neutralized gave a heavy brown precipitate of humin sub-

[1] Street, J. P., and Bailey, E. M., *J. Ind. Eng. Chem.*, 7, 853 (1915).

stance which contained no easily hydrolyzable carbohydrate. The dried insoluble portion represented 0.4% "crude fiber."

Organic Acids.—The heavy flocculent lead precipitate from the alcoholic extract was treated with hydrogen sulfide, and after removal of the lead sulfide and excess of hydrogen sulfide, was tested by the usual methods for a saponin body.[1] None was detected. The solution was acid. Citric acid had been identified by preliminary examination. The calcium precipitate obtained on the addition of calcium chloride was insoluble in either acetic acid or caustic soda, and the gelatinous precipitate obtained with barium hydroxide was insoluble in either dilute acetic acid or alcohol. Tests for malic and succinic acids showed negative results.

The free acid solution was titrated with decinormal alkali using phenolphthalein as indicator, and gave a mean of 19.2 cc. of alkali required to neutralize the acid from 50 g. of litchi, which is equivalent to 0.25% citric acid. The neutralized solution was then precipitated with barium chloride, the barium salt filtered off, dissolved in hydrochloric acid and the barium estimated as sulfate. The acid from 50 g. of litchi yielded 136 mg. of barium sulfate, which is equivalent to 0.21% of organic acid calculated as citric acid.

The small lead precipitate from the aqueous extract was treated in the same manner and yielded 85 mg. of $BaSO_4$, equivalent to 0.05% citric acid.

Acid- and Base-Forming Elements.—These were examined qualitatively by the methods of Sherman and Gettler.[2] Considerable amounts of calcium, magnesium, and iron were noted, and sulfate and phosphate ions were present in marked amount. No iodine was found when examined for by Hunter's method.

Glycogenetic Properties.—To confirm the results as to the nutritive value of the carbohydrate in the litchi, feeding experiments were conducted with rabbits according to the procedure carried out by Nakaseko[3] with inulin. After a 6-day fast 50 g. of litchi were fed and the animal killed within 16 hours. The liver was removed and the glycogen in it estimated by Pflüger's method with subsequent Allihn copper determinations.

Initial body weight	2040 g.
Final body weight	1820 g.
Duration of fast	6 days
Killed on the 7th day	..
Weight of liver	55.0 g.
Total glycogen found	5.86 g.
Glycogen in liver	10.7%

A control experiment was done, with a rabbit weighing 1900 g., which

[1] Haas, P., and Hill, T. G., "Chemistry of Plant Products," Longmans, Green & Co., London (1917).

[2] Sherman, H. C., and Gettler, A. O., *J. Biol. Chem.*, **11**, 323 (1912).

[3] Nakaseko, R., *Am. J. Physiol.*, **4**, 246 (1901).

after a 6-day fast weighed 1600 g. The animal was killed and no glycogen whatever was found in the liver.

These results show in a most marked way the glycogenetic properties of the carbohydrates in the litchi nut.

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[CONTRIBUTION FROM THE COMMERCIAL RESEARCH COMPANY, NEW YORK, AND THE MELLON INSTITUTE, PITTSBURGH.]

THE ACTION OF CONCENTRATED SULFURIC ACID ON OLEFINS, WITH PARTICULAR REFERENCE TO THE REFINING OF PETROLEUM DISTILLATES.

BY BENJAMIN T. BROOKS AND IRWIN HUMPHREY.

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The original object of the investigation discussed in the following paper was to throw some light on the reactions involved in the refining of petroleum distillates, as ordinarily carried out in petroleum refineries. We were at first somewhat handicapped by the fact that previous work on the behavior of the olefins to conc. sulfuric acid was practically limited to the first 4 members of the series, ethylene, propylene, butylene and the amylenes. The present contribution, we feel, does little more than open up the subject. However, certain facts seem amply demonstrated, and some of these facts vary widely from those to be expected from the commonly accepted theories.

The recent extensive development of cracking processes for the manufacture of light petroleum distillates from heavier oils has emphasized the desirability of studying the reactions involved in refining such light oils. Petroleum distillates have been refined almost exclusively by treating with conc. sulfuric acid since the very beginning of the petroleum industry; in fact Benjamin Silliman advocated such a procedure in his famous report made in 1855. The industry has apparently been quite content to accept the results of this operation, inasmuch as products so refined are generally acceptable to the users and no better refining method has, up to date, found general acceptance.

Although the action of dil. sulfuric acid, about 5% by volume, on a few olefins of the terpene series has been studied, a general investigation of the action of this, or other mineral acids on olefines has never been made; particularly is this true of the concentrated acids. The theory which has found practically universal acceptance in the petroleum industry is that the olefins occurring in petroleum distillates are polymerized by the acid to *tars*, form so-called "sulfo acids," and are completely removed from the oils so refined. That *this assumption is wrong* and that the so-called quantitative method of removing olefins by sulfuric acid gives misleading results will be brought out in the following