

The suggested method appears to give more true results than that of the A. O. A. C. determination and requires much less time. Only one gram samples were used, whereas five gram samples are required by the A. O. A. C.

SUMMARY

A method is suggested which is suited for the determination of free menthol in oil of peppermint and in menthol. The time required by the suggested method is about one-half of that for the U. S. P. XI method. The saponification step of the U. S. P. XI method, known to be a source of error, is eliminated, as is the washing of the acetylated oil with dilute sodium carbonate solution. An acetylant mixture of acetic anhydride and pyridine, itself quite stable, is used, esterifying the menthol in thirty minutes. Some evidence is presented which indicates that the U. S. P. XI method of acetylation affects other constituents of oil of peppermint besides menthol.

In the determination of esters in oil of peppermint, the addition of water after saponification was found to produce more

accurate results, as only one-third of the amount of indicator is required and the end-point is very sharp and easily observed.

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Some of the Constituents of the Tuber of Coqui (*Cyperus rotundus* L.). III.—The Sugars

By Conrado F. Asenjo*

The purpose of the present communication is to report on the sugars present in the alcoholic extractive obtained from the tubers of *Cyperus rotundus* L.

EXPERIMENTAL

Extraction and Clarification of the Molasses.—After having subjected the tubers to the process of extraction by continuous percolation with petroleum ether and ether, the marc left was subjected to extraction with 95 per cent alcohol. The alcoholic extractive, a dark brown syrup, amounted to 17.7 per cent of the air-dried tubers. Only part of this syrup was soluble in water; the rest, a resinous mass, remained insoluble. The water-soluble portion reduced Fehling's reagent very readily. After

slowly evaporating the water at a temperature of not over 50° C., a dark brown molasses remained which amounted to 50 per cent of the original alcoholic extractive. The molasses thus obtained was clarified by treating with basic lead acetate, neutral lead acetate and, finally, with vegetable charcoal. The excess lead was always precipitated with H₂S. The resulting molasses had a light caramel color.

Proximate Composition of the Molasses.—Reducing sugars were determined by the Drefren-O'Sullivan method (1), and amounted to 51 per cent of the molasses. Reducing sugars, after acid hydrolysis, 55 per cent. Non-reducing sugars by difference, 4 per cent. Aldoses determined by the Willstätter-Schudel titration (2), 41.7 per cent. As the molasses gave a positive Seliwanoff's test, the difference of 9.3 per cent between total reducing sugars and aldoses is probably made up of ketoses. The per cent of water in the molasses was 20 per cent. By difference, then, there was 25 per cent of substances which were neither sugars nor water in the clarified molasses.

* Guggenheim Memorial Fellow, Latin American Exchange, 1937-1939, Laboratory of Edward Kremers, Department of Pharmaceutical Chemistry, University of Wisconsin. Now Associate in Chemistry, School of Tropical Medicine, San Juan, Puerto Rico.

Characterization of the Sugars by the Usual Methods.—The molasses yielded very readily an osazone, m. p. 206–210° C., and a semicarbazone, m. p. 178° C. The second derivative, in particular, pointed to the presence of glucose. A methylphenylosazone, m. p. 167–168° C. was also obtained. Methylphenylfructosazone prepared by us from pure *d*-fructose melted at this same temperature.¹ No depression was observed in the melting point on mixing the two derivatives, therefore the presence of fructose was established.

Characterization of the Aldomonosaccharides in the Molasses as Benzimidazole Derivatives.—Following the procedure of Moore and Link (3), the aldomonosaccharides present in the molasses were oxidized to the corresponding aldonic acids and these, in turn, separated as K and Ba salts. These salts were then condensed with *o*-phenylenediamine to obtain the corresponding benzimidazoles.

Table I.—Constants of Benzimidazole Derivatives

Source	Benzimidazole m. p. (α_{D}^{25})	Hydro- chloride, Picrate, m. p.	m. p.
K salt from molasses	215	9.6	180 204
K salt from pure <i>d</i> - glucose	215	9.5	180 203
Ba salt from molasses	235	-49.0	230 156
Ba salt from pure <i>d</i> - arabinose	235	-49.1	230 158

The presence of *d*-glucose, as the principal sugar in the molasses, was further confirmed as large amounts of K *d*-gluconate were obtained. The isolation of a small amount of Ba salt, which yielded *d*-arabobenzimidazole when condensed with *o*-phenylenediamine, is indicative, as pointed out by Moore and Link (3), of the formation of *d*-arabinose from fructose during the oxidation pro-

¹ The melting point for methylphenylfructosazone reported in Browne's "Sugar Analysis," First ed., p. 622, as well as in other handbooks, is 158–160° C.

cedure. Therefore, *d*-arabinose is not present as such in the molasses. Its isolation in the form of a Ba salt only serves further to confirm the presence of fructose in the molasses, a fact already established by the preparation of the methylphenylfructosazone.

For the purpose of finding if small traces of benzimidazole derivatives have remained in solution in the filtrates, these were treated with a cupric ammonia solution as recommended by Moore and Link (3). The small amount of benzimidazoles, recovered from the Cu salts obtained from both filtrates, was found to be *d*-glucobenzimidazoles. It was concluded then that *d*-glucose was the only aldomonosaccharide present in the molasses.

SUMMARY

The molasses obtained from the alcoholic extractive of the tubers of *Cyperus rotundus* L. contains the following sugars: 41.7 per cent *d*-glucose, 9.3 per cent *d*-fructose and 4 per cent of non-reducing sugars. No other sugars could be detected.

The author is indebted to Professor Karl P. Link and Dr. Stanford Moore of the University of Wisconsin for detailed instructions for carrying out the characterization of the sugars by the benzimidazole procedure, which, at the time this investigation was undertaken, still was unpublished.

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The Patron Saints of Pharmacy*

By Leslie G. Matthews†

From the earliest times man has invoked the help of the supernatural—in prehistoric times no less than in the pagan and Christian eras. Those who in historic times early practiced the art of healing came in direct line from the tribal leaders and priest doctors whose healing powers derived partly from knowledge of their art and partly, if not mainly, from their power over others.

"Faith and works" have been nowhere more typically associated than in the sphere of medicine. Although cures depended upon faith in the personality of the healer, the reputation of the healer would often survive his times. Legends grew into a tradition until the stories became not merely those of simple cures but miraculous feats; associated not only with the healer but with his place of abode, the instruments of his art, his tomb, etc. This was certainly the case with the two chief patrons of pharmacy, St.

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† Pharmaceutical Chemist, London, England.