THE COMPOSITION OF GUM KARAYA

by

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# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Occurrence, Collection, Properties and Uses of Gum Karaya</td>
<td>8</td>
</tr>
<tr>
<td>Analysis of the Pure Gum</td>
<td>11</td>
</tr>
<tr>
<td>Hydrolysis of the Gum</td>
<td>14</td>
</tr>
<tr>
<td>Analysis of Barium Salt A</td>
<td>17</td>
</tr>
<tr>
<td>Separation and Identification of the Sugars</td>
<td>21</td>
</tr>
<tr>
<td>Conclusions</td>
<td>24</td>
</tr>
</tbody>
</table>
INTRODUCTION

Gums are one of the groups of substances found in plant life which are generally classed as carbohydrates. Various methods of classifying the carbohydrates are employed by different authors. Gortner\(^1\), in classifying them gives as group 4:

Polysaccharides or non-sugars

- a - Pentosans
- b - Methyl pentosans
- c - Hexosans
- d - Mixed pentosans
  - Gums
  - Mucilages
  - Hemicelluloses
  - Pectins
- e - Mixed hexosans
  - Celluloses
  - Etc.

The sub-group "mixed pentosans" have also been called polyuronides\(^2\) because, with the exception of some of the hemicelluloses, they all contain one or more uronic or sugar acids.

The mixed pentosans have generally been subdivided on the basis of the methods of extraction than on that of chemical composition, and the subdivisions are not sharply defined.

In general they consist of a rather long chain built-up of one or more uronic acids, one or more pentoses and one or more hexoses linked together. There are exceptions in the case of each of these constituents, for some of the hemicelluloses and at least one of the mucilages contain no uronic acid, at least one hemicellulose contains no pentose and a number of hemicelluloses contain no hexose material. Some of the hemicelluloses contain ether-linked methoxy groups on the uronic acid, and some have a group with indeterminate structure called an "X body." There is fair evidence that some pectins contain acetyl groups as well as ester-linked methoxies. Some other generalizations are possible. The uronic acids found in hemicelluloses are galacturonic and glucuronic, those in mucilages galacturonic and (in those from some mosses and marine algae) mannuronic. Pectins have shown only galact-

4. Buston and Chambers, Jour. Biochem. 27 (1933) 1691.
6. Ibid 41, 49.
7. Ibid 78.
8. Ibid 37.
uronic as the acid constituent, and the gums both glucuronic and galacturonic.

There is less uniformity in the kinds and relative amounts of sugars present. A comparison of all of the available studies made on gums shows L-arabinose and D-galactose to be always present, with sometimes a wide variety of other hexoses, pentoses or methyl pentoses.

Gums occur in nature as the exudation of scarified or diseased plants. Their origin in plants is not clearly established; some authorities suggest that they are normal products of plant metabolism while others believe that they result from the action of enzymes produced by fungi or by bacteria. In composition they are not clearly distinguished from mucilages nor some of the hemicelluloses, and at least some of them do not seem to have a constant uniform composition.

Neubauer did the first important chemical work on the gums in 1854, in a study of Gum arabic showing that it contained an acid constituent which he called "arabic acid" and which he believed to be a simple carbohydrate. In 1868 Scheibler decomposed this acid and obtained a sugar which he called "arabinose." O'Sullivan, in a series of

investigations on a number of gums (1880-1890) pointed out that they consist of a complex acid nucleus to which are attached sugar units which may be hydrolyzed off.\textsuperscript{11} It has since been shown that the uronic acids are the nuclear acids of these molecules and that they are present in nature as the calcium, magnesium or potassium salts, or as methyl esters of the complex acids.\textsuperscript{12} Also mesquite gum\textsuperscript{13} and lemon gum\textsuperscript{14} contain an ether-linked methoxy group attached to the uronic acid nucleus.

Gums are commonly divided into water-soluble and water-insoluble types. The former dissolves slowly to give a sticky solution while the latter swells up by imbibing many times its volume of water to give a thick viscid solution or gel.\textsuperscript{15} Among the water-soluble gums are gum arabic, mesquite gum and lemon gum while the insoluble type includes tragacanth, Karaya and cherry gums. More complete studies have been made on the former type chiefly because gum arabic is the most important commercially. There are several difficulties involved in studying the insoluble type since titrations, rotations of polarized light, and some other studies are impossible.

\textsuperscript{11} Ibid \textsuperscript{121.}
\textsuperscript{13} Otis, L., "The Constitution of Mesquite Gum" (1930).
\textsuperscript{14} Russell, F. H., "The Composition of Lemon Gum" (1931).
\textsuperscript{15} Norman, A. G., "The Biochemistry of Celluloses, the Poly-uronides, Lignins, etc." (1937) 121.
Gum arabic, it has been shown, is not homogeneous\textsuperscript{16}, and conflicting data on some other gums would indicate that some of the others are not. Van der Haar\textsuperscript{17} reports, for example, that gum tragacanth yields on hydrolysis l-arabinose, d-xylose, fucose, d-galactose, d-glucose, and d-galacturonic acid, while Norman\textsuperscript{18} reports only l-arabinose and a uronic acid. As the quality of some of the gums is known to vary with the season as well as place of growth and the length of time the plant has been producing gum, it is probable that the composition varies somewhat with these conditions.

Gum arabic has been studied by Norman and by Butler and Cretcher since the earlier work previously mentioned has been done. While the structure is still not definitely known, the approximate composition can be given. It consists of a nuclear galactosono-glucuronic acid, two galactose groups, three arabinose anhydrides and one methyl pentose\textsuperscript{19}, according to Butler and Cretcher. Norman did not find the methyl pentose l-rhamnose reported by the former\textsuperscript{20} and

\begin{itemize}
  \item \textsuperscript{16} Ibid 124.
  \item \textsuperscript{17} Van der Haar, A. W., "Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydesäuren, Gebruder Borntraeger. Berlin (1920).
  \item \textsuperscript{18} Norman, A. G., Biochem. Jour. 25 (1931) 200.
  \item \textsuperscript{19} Butler, C. L., and Cretcher, L. H., J. Am. Chem. Soc. 51 (1929) 1519.
  \item \textsuperscript{20} Norman, A. G., Biochem. Jour. 23 (1929) 524.
\end{itemize}
believes that it is not always present. His results would also indicate one less arabinose present. He believes that the linkage between the galactose and glucuronic acid of the nuclear aldobionic acid is of a different type than those between the rest of the sugars since it is so much more difficult to hydrolyze off.

Mesquite gum is of special interest because the structure is more completely known than that of any other gum and because it was the first gum studied in which an ether-linked methoxy group was found. It consists of a galactosomethoxy-glucuronic acid nucleus to which are attached two galactose units followed by four arabinose groups.\textsuperscript{21} It seems to be of uniform composition, all results being in remarkably close agreement.

Lemon gum was studied by F. H. Russell and found to consist of a galactosomethoxy-galacturonic acid nucleus combined with two units of galactose and one of \( l \)-arabinose in a long chain, the sequence being maintained through an undetermined number of repetitions.\textsuperscript{22}

Sands and Klaas, investigating cholla gum reported a rhamnoso-galacturonic acid nucleus linked to galactose and arabinose.\textsuperscript{23}

\textsuperscript{21} Otis, L., "The Constitution of Mesquite Gum" (1930).
\textsuperscript{22} Russell, F. H., "The Composition of Lemon Gum" (1931).
Cherry gum has been shown to yield on hydrolysis glucuronic acid, galactose, mannose, arabinose and xylose.24

It may be noted that a comparison of the constituents of the gums which have been studied shows that the galacturonic acid is found most often in the water-insoluble gums and glucuronic acid more frequently in the soluble gums. In fact no case of a water-soluble gum containing galacturonic acid was found although the reverse relationship showed exceptions.

OCCURRENCE, COLLECTION, PROPERTIES, 
AND USES OF GUM KARAYA

Gum Karaya, with which this paper is concerned, occurs as an exudation from trees of the family Sterculia Urens, a native tree of India, which is found chiefly in Gujerat, the Central Provinces, and to some extent in the Central India Agency. The gum is also known by the names Kadaya, Katila, and Kuloo, while commercially it is known as India Gum Tragacanth, or India Gum. This latter name should not be confused with Indian Gum, which is an alternate name for Gum Ghatti, and is so recognized in the British Pharmacopoeia.

The trees grow in large forests, most of which are government owned, although many are grown on the estates of large landowners. They reach a height of twenty-five to thirty feet, and their massive trunks are of a soft corky structure which cannot easily be burned.

Except during the rainy season the gum is obtainable at all times and is therefore usually collected by the natives at such times as there is a scarcity of farm work,

25. Information received through the courtesy of the Jacques Wolf Company, Passaic, New Jersey.
although the best quality of gum is obtained during the
cold weather which envelops the country from March to the
middle of June. Gum Karaya is collected only from the trunk
of the tree, in which the natives make incisions about two
feet long, and deep enough to reach the heart wood. Usually
five or six incisions are made in each tree, and the sap
or juice oozes out, collecting in large irregular knobs
in these incisions. In about three days these knobs are
dug out and new accumulations grow in the same wounds. If
the gum is not collected at these intervals, the wound
heals and new incisions must be made. After "bleeding"
for eight or nine months, the tree will yield no more gum
for two or three years, after which it can be tapped again
in new places.

The gum is collected and sacked by the natives and
sold to dealers in Bombay. All sorting and grading is done
in Bombay, usually by women, who break the large lumps with
stones and then sort these broken pieces into piles accord­
ing to color, etc. The grades run from dead white bald
pieces to which no bark adheres, down to small reddish­
brown pieces with large amounts of bark. These piles are
then collected and sacked according to grade.

In industry the chief use of gum Karaya is the util­
ization of its enormous swelling power when put into water.
A few grams will convert 200 or 300 cc. of water into a solid jelly-like mass in a few hours. This action is similar to that of gum tragacanth, and its first use was as a substitute for the latter. Its solution, however, differs in structure. Gum Karaya is more acid in odor and reaction. To make a coherent jelly it must be powdered to between 200 and 300 mesh, for a larger grinding results in a gel in which each of the swelled particles are distinguishable, while a very fine grinding weakens the swelling power. The gum has many uses in textile industries—as a printing agent, filler, sizing agent, and many others. It is also used in pharmaceutical preparations, in cosmetics, confectionery, and ice cream and other foods, and has recently been extensively used incorporated into liquid latex.
ANALYSIS OF THE PURE GUM

Analysis of the commercially purified gum showed the composition given in Table I.

Table No. I

Composition of Gum Karaya

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>3.68</td>
</tr>
<tr>
<td>Uronic acid</td>
<td>33.69</td>
</tr>
<tr>
<td>Pentose(^1)</td>
<td>8.78</td>
</tr>
<tr>
<td>Methyl Pentose(^2)</td>
<td>17.08</td>
</tr>
<tr>
<td>Total(^3)</td>
<td>63.23</td>
</tr>
</tbody>
</table>

1. Pentose calculated as araban
2. Methyl pentose calculated as rhamnosan
3. The difference cannot be calculated as hexose since qualitative tests indicate the presence of acetyl groups.

The calcium was determined by igniting samples to a white ash until the weight was constant. Qualitative examination showed that the ash was calcium carbonate. The presence of more than traces of any other metal was disproven as well as the presence of \(\text{PO}_4\)\(^2\) and \(\text{SO}_4\)\(^2\) groups. It was found that by continued strong ignition the carbonate could be converted to the oxide, the ratio of the
weights of samples of ash before and after the second ignition being in close agreement with the ratio of the molecular weights of CaCO₃ and CaO, respectively. From the weight of CaO found, the weight and per cent of calcium was calculated.

The uronic acid was determined by the method of Lefevre and the weight of carbon dioxide freed was multiplied by four to obtain the amount of acid lactone present.²⁶

The pentose was determined by the method recommended by the Association of Official Agricultural Chemists²⁷, but distillation was continued 20 or 30 minutes longer to insure complete conversion to, and separation of the furfural and methyl furfural. The filtering was done with sintered glass Jena crucibles provided with asbestos mats, as insurance against undue loss in the extraction with alcohol. The weights of the phloroglucides obtained were corrected for the amount yielded by uronic acids, since it has been shown that they give an appreciable error in pentosan determinations.²⁸ The pentosan was calculated from Krober's tables as araban.²⁸

²⁶. (a) Lefevre and Tollens, Ber. 40 (1907) 4513.
²⁷. A.O.A.C. Methods of Analysis (1925)
²⁸. Ref. 17.
The methyl pentose was determined by the Tollens-Ellett-Haywood method\textsuperscript{29} in which the weight of the phloroglucide extracted with alcohol from the total phloroglucide was considered to be the amount of methyl furfural phloroglucide originally present. The results were calculated from Ellett’s tables.\textsuperscript{28}

Additional tests were made for starch and for methoxy groups. A colloidal aqueous solution of the gum was tested with iodine solution and the absence of starch established. Both glucosidic and ether-linked methoxy groups were tested for with negative results, by methods described by Otis.\textsuperscript{30}

Since gum tragacanth\textsuperscript{31}, cherry gum\textsuperscript{32} and cholla gum\textsuperscript{33}, all gums of the insoluble type, could be fractionated into soluble and insoluble portions, an attempt to fractionate gum Karaya was made, but without success. No appreciable amounts of the gum were soluble in alcohol, ether, acetone, or mixtures of these solvents. Aqueous colloidal solutions, however, could not be precipitated with five or six volumes of alcohol, or with mixtures of alcohol and ether, to any

\textsuperscript{29.} (a) Browne, Handbook of Sugar Analysis (1912) 458.
(b) Ref. 17 67.
(c) Ellett and Tollens, Z. Deut. Zuckerind 42 (1905) 19.
\textsuperscript{30.} Otis, L., The Composition of Mesquite Gum (1930) 30.
\textsuperscript{31.} Ref. 15 129.
\textsuperscript{32.} Ibid 131.
\textsuperscript{33.} Klaas, R., The Composition of Cholla Gum (1927).
satisfactory degree, nor could a separation be made by centrifuging such a solution.

The odor of acetic acid was strong after samples of the gum were hydrolyzed with dilute sulfuric acid, so an attempt was made to prove the existence of acetyl groups in the gum molecule. The distillate of a mixture of dilute sulfuric acid and the gum was acid to litmus. When a small sample of the gum was heated in concentrated sulfuric acid a definite odor of acetic acid was given off, and when ethyl alcohol was added and the mixture boiled the fruity odor of ethyl acetate was detectable. However, an attempt to prepare acetonilide was unsuccessful, so the proof of the acetyl group cannot be considered as established, even though indications make it probable.

Hydrolysis of the Gum

A number of hydrolyses of the gum were made to determine the various hydrolytic products, and if possible, their relative positions in the molecule. These were carried out by heating a mixture of the gum and 4 per cent sulfuric acid on a boiling water bath, in a flask equipped with a condenser, for different periods of time, varying from three to seventeen hours. The gum and acid were mixed in the proportions of 50 grams of gum to one liter of acid, the
addition being made slowly and with frequent shaking, and the mixture was allowed to stand for at least twenty-four hours with vigorous shaking at intervals, in order to obtain as complete dispersion of the gum as possible.

The sulfuric acid was removed from the hydrolized solution by precipitation as barium sulfate with barium hydroxide and barium carbonate, care being taken not to let the solution become alkaline. This was then filtered off and the clear solution decolorized with Darco and concentrated by vacuum distillation on a boiling water bath. The concentrate was added to a large volume of 95 per cent ethanol, precipitating a barium salt which will subsequently be called Barium Salt "A." In some cases Barium Salt A was further fractionated on a basis of solubility by first adding the solution to two volumes of alcohol, precipitating out Barium Salt A₁. This was filtered off, and a much larger volume of absolute alcohol added, causing Barium Salt A₂ to precipitate. The filtrate from removal of Barium Salt A₂ was then concentrated down by distillation under a partial vacuum, which resulted in the precipitation of Barium Salt A₃. Small amounts of an even more soluble barium salt were separated by precipitation from the concentrated solution with hot absolute alcohol. This salt was called Barium Salt E.
The alcoholic solution from the extraction of the barium salts was then concentrated down to a syrup by distillation under a partial vacuum and the syrup dissolved in glacial acetic acid. This solution was then concentrated by vacuum distillation, seeded with galactose and left in a refrigerator for several days. The sugar which crystallized out was filtered out, and dried. The filtrate was concentrated further and the process repeated. When no more sugar could be crystallized out of the solution the acetic acid was swept out by distillation under vacuum with water. The residue was dissolved in water and purified with blood charcoal. It was then concentrated down again and taken up in absolute alcohol several times to remove any barium salt which might remain. No sugars could be crystallized from the syrup which remained after removal of the alcohol. The substance was dried and rotated, showing a specific rotation of \(+6^\circ\) which indicates low rotating sugars. Tests with Fehling's solution showed it to be strongly reducing.

The barium salt which was separated from the acetic acid solution was subsequently called Barium Salt B.
Analysis of Barium Salt A

The results tabulated below give average values for Barium Salt A from four separate hydrolyses. It is possible that the figure for pentose is too low since the correction made for furfuraldehyde from the uronic acid reduces it very much. Failure to make this correction, however, leaves the figure for galactose too low.

Table II
Composition of Barium Salt A.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Per cent found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uronic acid(^1)</td>
<td>41.23</td>
</tr>
<tr>
<td>Pentose(^2)</td>
<td>8.55</td>
</tr>
<tr>
<td>Methyl Pentose(^3)</td>
<td>13.30</td>
</tr>
<tr>
<td>Barium</td>
<td>20.26</td>
</tr>
<tr>
<td>Total</td>
<td>83.34</td>
</tr>
</tbody>
</table>

1. Calculated as \((\text{CO}_2 \times 4)\) uronic anhydride
2. Calculated as araban
3. Calculated as rhamnosan

Since galactose was identified as one of the products of the rehydrolysis of Barium Salt A it may be presumed to account for the 16.66 per cent difference in the above table. The specific rotation of Barium Salt A was \([\alpha]_D^{\infty} = +68.8^\circ\). The above figures would indicate that Barium Salt A is either a very large molecule, or, more probably, that it is
a mixture of salts. Fractionation of the salt, on the basis of solubilities as previously described show the following results for the fractions, arranged in the order of increasing solubility.

Table III

A Comparison of the Barium Salts

<table>
<thead>
<tr>
<th>Barium Salt</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>D1</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Per cent Uronic Acid</td>
<td>44.88</td>
<td>41.60</td>
<td>15.44</td>
<td>7.60</td>
<td>5.36</td>
</tr>
<tr>
<td>Per cent Barium</td>
<td>21.57</td>
<td>20.08</td>
<td>36.21</td>
<td>41.17</td>
<td>48.50</td>
</tr>
<tr>
<td>Per cent Pentose</td>
<td>8.50</td>
<td>15.99</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>Per cent Methyl Pentose</td>
<td>10.50</td>
<td>11.3</td>
<td>6.60</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td>Totals</td>
<td>85.45</td>
<td>88.97</td>
<td>58.25</td>
<td>49.77</td>
<td>53.86</td>
</tr>
<tr>
<td>Specific Rotations</td>
<td>+61.4°</td>
<td>+72.2°</td>
<td>+30.8°</td>
<td>+14.4°</td>
<td>+21.57°</td>
</tr>
</tbody>
</table>

1. Barium salt D was precipitated with absolute alcohol from a concentrated solution. Only a very small amount of this salt was separated.

One striking fact is notable from a comparison of the salts—with increasing solubility there is a steady decrease in amount of uronic acid, yet an increase of barium. This would indicate the existence of another acid, the barium salt of which is very soluble in water, or of a more complex barium-sugar compound. Previous indications of acetic
acid made it probable that this was the acid present. This would conform fairly well to the amount of barium present and to the fact that some of it was precipitated from the hot solution after previous treatment of the cold solution, for barium acetate is less soluble in hot water than in cold water. Treatment of Salt E with sulfuric acid gave a definite acetic acid odor, and addition of ethanol gave the characteristic odor of ethyl acetate.

Comparison of Salt A<sub>1</sub> with Salt A<sub>2</sub> indicates that an increase in pentose results in an increase in solubility. The higher percentage of arabinose in Salt A is substantiated by the increase in specific rotation, even when allowance is made for the lower barium content. Relatively little separation according to constituents is revealed, however, and satisfactory methods of effecting such separation were not developed. Each of the fractions was apparently a mixture of a fairly large number of compounds.

Barium Salt B, which was precipitated after treatment with acetic acid, was not included with the above salts because its very high barium content—up to fifty percent—and positive tests for acetate indicate that it is barium acetate, possibly formed from the glacial acetic acid used to separate out the sugars.
Varying the length of the period of hydrolysis, and subsequent rehydrolysis of the barium salts showed that some of each of the three sugars present remained attached to the uronic acid units even with long periods, when analysis shows the ratio of uronic acid units to sugar units to be approximately one to one. This would indicate direct linkages between each of the sugars and uronic acid units.

Efforts to hydrolyze off the sugars from the uronic acid were unsuccessful. When hydrolysis was carried out under pressure in an autoclave the uronic acid was decomposed. Prolonged hydrolysis on a boiling water bath detached some sugar units, chiefly galactose but also some arabinose and rhamnose, but no pure uronic acid could be obtained. Consequently the acid could not be identified.
SEPARATION AND IDENTIFICATION OF THE SUGARS

The only sugar which could be obtained in a nearly pure state was d-galactose. It was crystallized out of the sugar concentrate after removal of the barium salts, after seeding and refrigeration. The identification was made by its rotation of polarized light and by oxidation to mucic acid with nitric acid by the method described by Van der Haar. Various samples extracted from separations of the products of different hydrolyses gave specific rotations varying from +72.67° to +83.10° not corrected for moisture. In each case the solution prepared for rotation contained a drop of ammonium hydroxide to prevent mutarotation. The melting points of the various samples of mucic acid ranged from 210° to 216°C.

In general the galactose was much more easily separated than the other sugars chiefly because of its greater abundance.

The 1-rhamnose was never obtained separately. Its identification depends chiefly on the study of a coarse crystalline sugar obtained from the products of the re-hydrolysis of Barium Salt A. This sugar showed a specific

34. Ref. 17
rotation of \([\alpha]_D^{25} = +52.10\). Rosenthaler's test showed the presence of a methyl pentose\(^{35}\) and tests with skatole solution proved the presence of a hexose.\(^{36}\) Treatment with nitric acid yielded mucic acid, proving the hexose to be galactose. Quantitative determinations for methyl pentose and pentose\(^{37}\) showed no pentose and 47.5 per cent methyl pentose. If the substance were an equimolecular mixture of galactose and rhamnose this percentage would be obtained, and also the above specific rotation. It reduced Fehling's solution strongly and fermented with yeast fairly well after seven or eight hours, proving it to consist of aldose sugars. CO\(_2\) determinations and qualitative barium tests proved the absence of any uronic acid. The melting point of the sugar was 98°-99°C.

The melting point of a mixture of pure 1-rhamnose and d-galactose consisting of 47.5 per cent rhamnose and 52.5 per cent galactose gave a melting point of 97°-99°. A mixture of the sugar with the synthetic mixture gave a melting point of 96°-98°. Since fucose, the only other naturally occurring methyl pentose has a specific rotation of +75°, any combination of it with galactose could not give the rotation found for the sugar. While not absolute proof,

\(^{35}\) Dische und Popper, Biochem. Zeitschrifte \textbf{175} (1926) 371.
\(^{37}\) Ref. 27.
together these findings give fairly conclusive evidence that l-rhamnose is present.

The separation of l-arabinose could only be made after first removing galactose from the sugar solution remaining from the hydrolysis mixture after removal of the barium salts. Only a small amount was obtained and this was not pure. The identification is not conclusive, depending on proof of the presence of a pentose in the pentosan determinations made together with the specific rotation of the fraction separated. This was found to be \( [\alpha]_D^{25^\circ} = +93.0 \) Ammonia was used to prevent mutarotation. No other sugars found, nor mixture of them could show a rotation this high, so the assumption was made, after tests with Fehling's solution proved it to be reducing, and a test with skatole solution indicated a pentose, that the sugar was l-arabinose. This should be confirmed by other tests before the presence of l-arabinose can be positively established.
CONCLUSIONS

Gum Karaya contains pentose, methyl pentose, galactose, and a uronic acid which is probably acetylated.

The galactose was identified as the dextro-rotating form and the pentose and methyl pentose are probably l-arabinose and l-rhamnose, respectively, but further proof of identification is necessary.

These units are linked together in a long chain of high molecular weight in a proportion which makes a homogeneous compound unlikely.
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