Gum Ghatti (Indian Gum). The Composition of the Gum and the Structure of Two Aldobiouronic Acids derived from it.

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Gum ghatti on hydrolysis yields a mixture of L-arabinose (5 mols.), D-galactose (3 mols.), D-mannose (1 mol.), xylose (½ mol.), D-glucuronic acid (1 mol.), and traces (below 1%) of methylpentose. On graded hydrolysis the gum gives two aldobiouronic acids, namely 6-*O*-β-D-glucuronosyl-D-galactose and 2-*O*-β-D-glucuronosyl-D-mannose. Oxidation of the gum with periodate has been studied.

The chemistry of gum ghatti (Indian gum) from *Anogeissus latifolia*, Wall (family, Combretaceæ), was investigated by Hanna and Shaw (*Proc. S. Dakota Acad. Sci.*, 1941, **21**, 78) who reported the presence of pentosan (50%) and galactose or galacturonic acid (12%) in the gum. They isolated L-arabinose after partial hydrolysis with acid and obtained a resistant aldobiouronic acid of equivlaent weight 352. In the present work a beginning has been made in the study of the detailed molecular structure of this important gum.

A purified sample of the gum had an equivalent weight of about 1600 (by titration with alkali) and on complete hydrolysis yielded L-arabinose, D-galactose, D-mannose, and D-glucuronic acid. Some xylose and a trace of methylpentose were also present but it is not certain whether these residues are present in the molecular structure.

The uronic anhydride content, determined by the carbon dioxide liberated by 19% hydrochloric acid at 145° (McCready, Swenson, and Maclay, *Ind. Eng. Chem. Anal.*, 1946, **18**, 290), was 12·0% (calculated for a substance of equivalent weight 1600, 11·0%). The pentosan content of the gum acid was 46·4%, calculated as anhydroarabinose from the liberated furfuraldehyde determined as thiobarbiturate (Marshall and Norris, *Biochem. J.*, 1937, **31**, 1293), account being taken of the furfuraldehyde yielded by the uronic acid residues (Norris and Resch, *Biochem. J.*, 1935, **29**, 1590).

After complete hydrolysis of the gum, determinations of the sugars separated on paper

chromatograms were carried out by the periodate method (Hirst and Jones, *J.*, 1949, 1659). The following results were obtained: arabinose 41·1%, xylose 2·7%, galactose 26·7%, mannose 8·3%, the figures in each case being calculated for the anhydro-sugar residue.

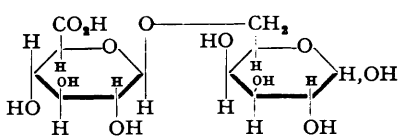
A gum acid with equivalent weight 1600 consisting of 5 arabinose residues, 3 galactose residues, 1 mannose residue, and 0·5 xylose residue per unit of uronic anhydride, would contain the following percentages of anhydro-sugars: arabinose 41·2% (found, 41·1%), galactose 30·4% (found, 26·7%), mannose 10·1% (found, 8·3%), xylose 4·1% (found, 2·7%), uronic anhydride 11·0% (found, 12·0%).

When the gum acid was boiled in aqueous solution 4 moles of L-arabinose per equivalent were readily removed, probably because they are present in the furanose form and located in the outer parts of the molecule. The remaining arabinose residue was less easily removed by autohydrolysis, leaving a resistant degraded gum containing some 4% of arabinose residues possessing an equivalent weight of about 1000.

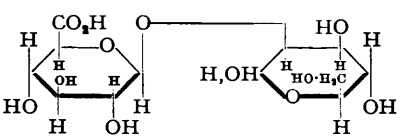
On reaction with periodate, 80% of the arabinose residues in the gum acid are oxidised; on the other hand, only about one third of the galactose residues are attacked. During the reaction *ca.* 3 moles of formic acid are produced per equivalent. These results are understandable if 80% of the arabinose residues in the gum molecule possess adjacent hydroxyl groups and are present as L-arabofuranose residues linked through $C_{(1)}$ and $C_{(5)}$. It is probable that the L-arabinosyl linkages are α in type, since on partial hydrolysis, the specific rotation changes from $[\alpha]_D$ −48° for the gum acid to +6° for the degraded gum. It also follows that most of the galactose residues are engaged in linkages such as $C_{(1)}$–$C_{(3)}$ which exclude the presence of contiguous hydroxyl groups. In this connection it will be recalled that D-galactopyranose residues linked through $C_{(1)}$ and $C_{(3)}$ have been encountered in most of the plant gums previously examined. In view of the amount of formic produced during the oxidation with periodate it is likely that the D-galactose residue which is attacked is linked through positions $C_{(1)}$ and $C_{(6)}$.

After partial hydrolysis of the gum acid with aqueous sulphuric acid a product containing two aldobiouronic acids was obtained. One of these contained D-mannose and a uronic acid whilst the other liberated D-galactose on further hydrolysis. Proof of their structure was obtained by methylation of the mixture of aldobiouronic acids and subsequent examination of the methylated sugars liberated on hydrolysis. The uronic acid fraction was then identified as 2 : 3 : 4-tri-*O*-methyl-D-glucuronic acid after conversion into the crystalline methyl ester of 2 : 3 : 4-tri-*O*-methyl-D-saccharolactone. The neutral fractions were 3 : 4 : 6-tri-*O*-methyl-D-mannose and 2 : 3 : 4-tri-*O*-methyl-D-galactose, identified by their rates of movement on chromatograms and by their properties after isolation in the crystalline state.

The portion of the gum molecule most resistant to hydrolysis consists therefore of two aldobiouronic residues, namely 6-*O*-β-D-glucuronosyl-D-galactose (I) and 2-*O*-β-D-glucuronosyl-D-mannose (II), which appear to be present in approximately equal proportions, since the ratio galactose : mannose was 1 : 1 in the mixture of aldobiouronic acids obtained after partial hydrolysis of the gum with 0·16N-acid. The specific rotation of the methylated aldobiouronic acids indicates that the glucuronosyl junction is β in type.



(I)



(II)

In respect of the constituent sugars, gum ghatti resembles damson gum (Hirst and Jones, *J.*, 1938, 1174) and cherry gum (Jones, *J.*, 1939, 558), both of which are built up of residues of D-glucuronic acid, L-arabinose, D-xylose, D-galactose, and D-mannose. All three gums yield on partial hydrolysis the same aldobiouronic acid, 2-*O*-β-D-glucuronosyl-D-mannose (II). Gum ghatti and cherry gum show further similarity in the large proportion of L-arabinose residues present in their molecular structures, but much more work with both gums will be necessary before a detailed structural comparison will be possible.

It is of interest in this connection that gum ghatti gives also on partial hydrolysis another aldobiouronic acid, namely 6-*O*-β-D-glucuronosyl-D-galactose (I) which is a characteristic feature of gum arabic and other gums of the *Acacia* group.

Experimental

Purification of the Gum.—The commercial sample of gum ghatti (obtained from Messrs. Eimer and Amend, New York) consisted of yellowish nodules, soluble in water with the exception of a few fragments of bark, etc. The aqueous solution gave a positive test for calcium. The gum acid was precipitated by pouring a filtered aqueous solution of the gum into ethanol, acidified with hydrochloric acid to about 0·1N. The precipitate was purified by the method described for damson gum (Hirst and Jones, *J.*, 1938, 1174) and was dried at 40—50° under reduced pressure.

It was noticed that during the precipitation a small portion of the gum acid (*ca.* 2%) separated as a finely dispersed suspension. This was separated, after addition of ether to the mixture, and showed the same analytical properties (equivalent weight, optical rotation, pentosan content) as the main batch, and on complete hydrolysis it liberated the same sugars. It appeared therefore to be identical with the main portion.

Analysis of the Purified Gum Acid.—The figures given below are mean values from a series of analyses carried out with two separately prepared batches; no significant difference in properties was observed between the two preparations: $[\alpha]_D^{20}$ −50° (approx.) (as Na salt; *c*, 1·0 in H_2O); equivalent weight by acid acidimetry, 1600; carbon dioxide liberated when heated with 19% hydrochloric acid, 2·99% (corresponding to 12·0% uronic anhydride) (calc. for a polysaccharide of equiv. wt. 1600: CO_2, 2·75%, uronic anhydride, 11·0%); pentosan content, 46·4% (as anhydroarabinose; calc. from the amount of furfuraldehyde evolved under standard conditions); ash (as sulphate), <0·5%; N_2 (Kjeldahl), <0·4%; acetyl groups, <0·4%. The gum acid had an apparent methoxyl content (Zeisel estimation), 2·2%; but this was probably due to esterification during the precipitation by acid ethanol. The crude gum had a negligible OMe content (<0·1%). A small iodine number observed with the purified gum acid (5·6 ml. of 0·1N-iodine per 1·0 g.) may also be due to ethyl alcohol introduced during the purification. The gum acid did not reduce Fehling's solution.

Examination by Paper Chromatography of the Sugars produced on Complete Hydrolysis of the Gum Acid.—A solution (0·5%) of gum acid in 2N-sulphuric acid was heated for 24 hr. in a sealed tube immersed in a boiling-water bath. The solution was neutralised (Amberlite IR-4B) and then concentrated under reduced pressure. On chromatograms including reference substances and run with several solvent systems, the four sugars, galactose, mannose, arabinose, and xylose, were detected. Spots corresponding to more resistant parts of the gum (*e.g.*, oligosaccharides) were not observed. Another solution, obtained as described above, was neutralised by barium carbonate, followed by removal of the barium neutral filtrate by Amberlite IR-120. The solution was then concentrated under reduced pressure and examined on paper chromatograms obtained under the conditions described for the detection of uronic acids (Partridge, *Biochem. J.*, 1948, 42, 238). Spots corresponding to glucuronic acid and glucurone were observed.

Quantitative Determination of the Sugars present in the completely Hydrolysed Solution.—After paper-chromatographic separation of the sugars, their quantities were determined by the periodate method (Hirst and Jones, *J.*, 1949, 1659), D-ribose being used as reference sugar. The figures are mean values from a series of chromatograms and indicate the proportions (calculated as anhydro-sugars) obtained from 100 parts of intact gum acid; galactose, 26·7%, mannose, 8·3%, arabinose, 34·0%, xylose, 2·7%.

These figures plus 11·0% uronic anhydride fall short of 100% and it was evident that decomposition had taken place during the hydrolysis. This is mostly due to loss of pentose since the figure for anhydroarabinose by the furfuraldehyde method was 46·4%. Subsequent experiments showed that most of the pentose is liberated during 60 min. in the sealed-tube experiments. It follows that the free arabinose was submitted to more than 20 hours of heating in a boiling-water bath in an acid medium. As shown in the following section it is, however, possible by using milder conditions of hydrolysis to obtain quantitative results for arabinose which are in good agreement with the furfuraldehyde determination.

Quantitative Determination of Arabinose after Autohydrolysis of the Gum Acid and after Hydrolysis of the Gum with 1·0N-*Formic Acid.*—A 2% aqueous solution of gum acid was heated

in a boiling-water bath until the optical rotation became constant at $[\alpha]_D^{20}$ +49° after 44 hr. Paper chromatography showed that, in addition to the liberated arabinose and traces of xylose, galactose began to split off after 44 hr. Determination of the arabinose on the chromatograms showed that an amount corresponding to 34·4% of anhydroarabinose, or 4 residues per equivalent weight (1600), was liberated.

Hydrolysis of the gum acid with N-formic acid in a boiling-water bath for 20 hr. proceeded with little apparent decomposition. The hydrolysis products were separated chromatographically. As in the case of the autohydrolysis, xylose and galactose were liberated in amounts too small for accurate determinations. (*A*) Gum acid (544·6 mg.) and D-ribose (199·5 mg.) were dissolved in N-formic acid (10 ml.) and refluxed in a boiling-water bath for 20 hr. Arabinose liberated: 42·7% (calc. as anhydroarabinose). This amount did not increase during continued heating in 3N-formic acid. (*B*) D-Ribose (175·8 mg.) was added after the hydrolysis (20 hr.) of gum acid (573·0 mg.) in N-formic acid (10 ml.). Arabinose liberated: 39·5% (calc. as anhydroarabinose). It is likely that method (*A*) will give results slightly above the correct figure, whereas method (*B*) probably involves a slight error in the opposite direction. The mean value (41·1%; corresponding to 5 residues of arabinose per equiv.) is in reasonable agreement with the results of the furfuraldehyde determination (46·4%) when account is taken of the presence of xylose (*ca.* 3%) and rhamnose (*ca.* 1%) residues.

Examination of the Degraded Gum.—An aqueous solution of the gum acid was heated for 48 hr. in a boiling-water bath ($[\alpha]_D^{20}$ +49°). It was then filtered and concentrated to a thin syrup at 40—50° under reduced pressure. The syrup was poured into ethanol, and the precipitated polysaccharide washed repeatedly with hot methanol and dried at 40° under reduced pressure (yield 25%). It had $[\alpha]_D^{20}$ +6° (as sodium salt; *c*, 1·0 in H_2O); equiv. (by acidimetry), 985; equiv. (by determination of uronic anhydride), 977. Pentosan, calculated as anhydroarabinose, 3·7%, from furfuraldehyde determinations.

Determinations were made after paper-chromatographic separation of the sugars liberated on complete hydrolysis of the degraded gum (by heating it with 2N-sulphuric acid for 24 hr. in a sealed tube immersed in a boiling-water bath). The following mean values were obtained (calc. as percentage of anhydro-sugar in the intact degraded gum): galactose, 48·5%; mannose, 11%; arabinose, 3·5%; xylose, 1%. Account being taken of the presence of 17·2% of uronic anhydride, the total is less than 100%, owing probably to decomposition during hydrolysis. Approximately one sugar residue per equivalent is missing.

Isolation of L-*Arabinose and* D-*Galactose, by Stepwise Hydrolysis of the Gum Acid.*—L-*Arabinose.* After autohydrolysis and precipitation of the degraded gum acid, the mother liquor was concentrated under reduced pressure to a thick syrup, which was repeatedly extracted with boiling ethanol. The combined alcoholic extracts on concentration yielded crystalline L-arabinose (yield 10%), still contaminated with traces of xylose, but after recrystallisation from ethanol the substance was chromatographically homogeneous and then had m. p. and mixed m. p. 156—158°, $[\alpha]_D^{20}$ +103° (*c*, 1·0 in H_2O).

D-*Galactose.* Degraded gum acid was partly hydrolysed with sulphuric acid (2N) in a boiling-water bath. After 4 hr. the solution was neutralised with barium carbonate, filtered, concentrated (reduced pressure), and poured into ethanol. The barium salts were filtered off and the mother liquid was concentrated (reduced pressure) to dryness. On trituration of the residue with hot methanol crystalline D-galactose separated (yield 2%); chromatographically pure it had m. p. and mixed m. p. 162—165°. Further evidence that this was the D-isomer was provided by the isolation of *O*-methyl-D-galactoses on hydrolysis of the methylated degraded gum (unpublished results).

Oxidation of the Gum Acid by Periodate.—Portions (10 ml.) of an aqueous solution (0·0025N; neutral to methyl red) of the sodium salt of the gum acid were allowed to react with sodium metaperiodate (0·05M; 10 ml.) at room temperature in the dark. The periodate uptake was determined by the arsenite method, and the formic acid by titration with aqueous sodium hydroxide (methyl red as indicator) after addition of ethylene glycol. The following results were obtained as mean values of two series of analysis:

Time (hr.)	2	4	8	20	48	60	96
Periodate reduced (moles)	7·0	8·4	9·1	9·9	10·5	10·7	10·8
Univalent acid liberated (moles)/equiv. of gum acid	2·5	2·8	3·0	3·1	3·3	3·4	3·4

Examination of the Material remaining after Oxidation of the Gum with Periodate.—Preliminary qualitative determinations showed that some galactose, mannose, and arabinose still remained intact in the oxidised gum. But neither uronic acid nor xylose could be detected.

Gum acid (270 mg.) was oxidised with sodium metaperiodate (700 mg.) for 48 hr. The oxidation was stopped by the addition of ethylene glycol, and the solution was then dialysed against running water until inorganic ions had been removed (5 days). The solution was concentrated (reduced pressure) to about 30 ml., made acid (2N) with sulphuric acid, and heated for 20 hr. at 98°. It was neutralised with barium carbonate, and the concentrated filtrate was examined on paper chromatograms. Analyses showed that the following sugars were present : arabinose, 9·2% ; galactose, 20·8% ; mannose, 7·1% (the figures give the amount of each sugar remaining unoxidised expressed as percentages of the weight of the original gum acid).

Examination of the Product obtained by Graded Hydrolysis of the Gum.—Hydrolysis of the gum with aqueous sulphuric acid could not be followed beyond the early stages polarimetrically or by determination of the iodine number, since even with 0·16N-acid considerable destruction took place (brown colour and precipitate). After 24 hr. at 100°, the solution was neutralised and the acidic materials were isolated as the barium salts [Yields : (*a*) Product *A* from hydrolysis with 0·16N-acid ; 15% with Ba content, 18·6%. (*b*) Product *B* from hydrolysis with 0·5N-acid ; 8% with Ba content, 23·0%. (*c*) Product *C* from 0·9N-acid ; 1·5%]. All three products liberated glucuronic acid, galactose, and mannose on further hydrolysis. Quantitative paper-chromatography showed that galactose and mannose were liberated in equimolecular proportions from product *A* and in the ratio 1 : 1·5 from product *B*. The barium content is too high to account for the presence of a trisaccharide (aldotriouronate) or a mixture of an aldobiouronic acid and a resistant oligosaccharide (barium calc. for aldobiouronate, 16·2% ; for aldotriouronate, 11·7%).

Barium ions were removed from an aqueous solution, with Amberlite IR-120, and the resulting solution was examined on paper-chromatograms run with the solvent systems (I) (amyl alcohol–pyridine–water ; 7 : 7 : 6), and (II) (ethyl acetate–formic acid–acetic acid–water ; 18 : 1 : 3 : 4) (both systems, " one-phase "). Two spots showing reducing and acid properties (bromophenol blue) were observed, moving at rates characteristic of disaccharides ; in solvent (I) $R_{galactose}$, 0·45 and 0·55 (galactose, 1·00) ; in solvent (II) $R_{glucurone}$, 0·14 and 0·23 (glucurone 1·00). Glucuronic acid which is present in traces was clearly separated from the other spots in system (II).

Chromatograms with larger quantities of product *A* were run [solvent (I)] on thick paper (Whatman 3MM). The two spots were eluted and on hydrolysis of the eluates the upper spot yielded glucoronic acid and galactose whereas the lower spot yielded glucuronic acid and mannose (paper-chromatography). Final proof of the presence of two distinct aldobiouronic acids in the mixture emerged from the methylation studies described below.

Large-scale Preparation of the Barium Aldobiouronates.—Gum acid (100 g.) was dissolved in 0·45N-sulphuric acid (2 l.) and heated in a boiling-water bath for 24 hr. The filtered solution was neutralised with barium carbonate (150 g.) at 80° with stirring, and the liquid portion was decanted, centrifuged, and concentrated at 40—50° (reduced pressure) to a syrup which was poured into alcohol. The precipitated barium salts were washed with hot alcohol (crude yield, 25 g.), purified by 3 successive precipitations and washed with alcohol (yield, 10 g.) [Found : OMe, negligible ; adsorbed free sugars (by paper-chromatography)—traces of galactose and arabinose, and traces of glucuronic acid (all below 1%) ; Ba, 23·0% (calc. for barium aldobiouronate, 16·2%) ; uronic anhydride, 44·0% (calc. for barium aldobiouronate, 41·5%) ; galactose (as anhydro-sugar), 15·8% ; mannose (as anhydro-sugar), 23·7% ; (both determined by paper-chromatography after hydrolysis)]. The total hexose anhydride is therefore 39·5% (calc. for a barium aldobiouronate, 38·2%).

Isolation of a Methylpentose as Hydrolysis Product.—The alcoholic washings from the large-scale preparation of the barium salts of aldobiouronic acids (see previous section) were concentrated to dryness under reduced pressure. The product gave on chromatographic examination, in addition to the spots expected, a weak spot which moved at the rate of rhamnose. Determination by Nicolet and Shinn's method (*J. Amer. Chem. Soc.*, 1941, **63**, 1456) showed the presence of methylpentose in amount corresponding to about 1% of the gum.

Methylation of the Aldobiouronic Acids.—The barium salts (9 g.) were dissolved in water (100 ml.) and methylated three times with dimethyl sulphate and sodium hydroxide in an atmosphere of nitrogen with vigorous stirring. (1) Dimethyl sulphate (100 ml.) was added and then sodium hydroxide (200 ml. ; 30%) dropwise at a temperature below 30°. (2) Solid sodium hydroxide (50 g.) was dissolved in the mixture the following day and dimethyl sulphate (100 ml.) was added dropwise at a temperature below 35—40°. The mixture was heated for 30 min. on a boiling-water bath, cooled, partly neutralised (H_2SO_4), and filtered. (3) The concentrated (at reduced pressure) filtrate was again methylated by dimethyl sulphate (50 ml.)

and sodium hydroxide (100 ml.; 30%) at below 40°. The mixture was finally heated to 80° for 30 min., cooled, acidified with sulphuric acid, and repeatedly extracted with chloroform. The combined extracts were concentrated to a syrup under reduced pressure, and the residue (5 g.) was further methylated with methyl iodide and silver oxide. The product (a yellow, viscid syrup; 4·7 g.) was distilled, giving the following fractions (temperatures are those of the heating bath): (I) a bright yellow, mobile syrup (0·80 g.), b. p. 185—190°/0·1 mm. (Found: OMe, 49·8%); (II) nearly solid, brownish yellow (1·4 g.), b. p. 200°/0·03 mm. (Found: OMe, 49·9%), $[\alpha]_D^{20}$ −24·2° (*c*, 5 in MeOH); (III) residue, b. p. >230°/0·03 mm. (Found: OMe, 50·1%).

Samples of the fractions were hydrolysed and the methylated sugars liberated were examined on paper-chromatograms. None of the fractions gave tetramethylgalactose or tetramethylmannose. Fraction II gave spots of methylated uronic acid, trimethylgalactose, R_G 0·65, and a trimethylmannose, R_G 0·80. Fraction I gave mainly methylated uronic acid and traces of the two trimethyl sugars. The residue (fraction III) gave the same spots as fraction II, but in addition there were two unidentified sugars (traces only), having R_G 0·50 and 0·78, respectively.

Separation and Identification of the Hydrolysis Products of the Methylated Aldobiouronic Acids (Fraction II).—Fraction II (1·2 g.) was hydrolysed with N-sulphuric acid (25 ml.) for 13 hr. in a boiling-water bath. The solution was neutralised ($BaCO_3$), filtered, and evaporated, leaving a yellowish powder (1·0 g.), which was exhaustively extracted with dry ether. The product was a chromatographically-homogeneous barium salt of methylated glucuronic acid (*Y*) (0·50 g.).

The ethereal extract on evaporation gave a yellowish syrup (*X*) (0·50 g.), which was separated into its constituents on cellulose (working dimensions, 2·5 × 75 cm.), *n*-butanol–light petroleum (b. p. 100—120°) (30/70 by vol.), saturated with water, being used as mobile phase. The eluate was collected in portions (6—7 ml.), and two fractions were obtained: (i) (0·10 g.), 3 : 4 : 6-tri-*O*-methyl-D-mannose, R_G 0·80, m. p. and mixed m. p. 101—102°, $[\alpha]_D^{20}$ +10° (*c*, 2 in H_2O); (ii) (0·05 g.), 2 : 3 : 4-tri-*O*-methyl-D-galactose, R_G 0·64 (Hirst and Jones, *Discuss. Faraday Soc.*, 1949, **7**, 271). Fraction (ii) crystallised as the hydrate when kept. After recrystallisation from ether, it had m. p. 78°, with some sintering at 73° (see Smith, *J.*, 1939, 1734) and showed a large depression of m. p. when mixed with 2 : 4 : 6-tri-*O*-methyl-D-galactose (R_G 0·67).

The barium salt (*Y*) was dissolved in water, and barium ions were removed with Amberlite IR-120. The tri-*O*-methyl-D-glucuronic acid remaining in solution was oxidised with bromine water to 2 : 3 : 4-tri-*O*-methyl-D-saccharic acid (0·25 g.) which was esterified with methanolic hydrogen chloride. The ester was distilled (b. p. 160°/0·3 mm.); the distillate ($[\alpha]_D$ positive) crystallised when nucleated with the methyl ester of 2 : 3 : 4-tri-*O*-methyl-D-saccharolactone, m. p. and mixed m. p. 109—110°. The two aldobiouronic acids obtained by partial hydrolysis of the gum are therefore 2-*O*-β-D-glucuronosyl-D-mannose and 6-*O*-β-D-glucuronosyl-D-galactose.

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