ALKYL OLIGOSACCHARIDES AND THEIR MIXTURES WITH ALKYL GLUCOSIDES AND ALKANOLS

ABSTRACT OF THE DISCLOSURE

Surface active alkyl oligosaccharides and mixtures of alkyl oligosaccharides with alkyl glucosides and alkyl alcohols are prepared from an alkyl and glucose via a trans-acetalation reaction. Preparation of these compositions may be carried out by reacting glucose and a lower alkyl in the presence of an acid catalyst to form a mixture of lower alkyl glycosides which are then reacted with higher alkyls to form the desired products.

This invention concerns surface active alkyl oligosaccharides, and mixtures of alkyl oligosaccharides with alkyl glucosides and alkyl alcohols, as well as processes for their preparation.

In particular, the invention is concerned with the preparation of alkyl oligosaccharide mixtures whose components have the structure RO(C₆H₄OH)₉H where R is selected from the group consisting of aliphatic hydrocarbon radicals ranging from C₃H₇ to C₆H₁₄. In the oligosaccharide portion, —O—(C₆H₄O)₉H₂, is at least 2, but averages 3 or more, glycosyl units. One of the glycosyl units is connected through its first carbon atom to the alkyl group. —R—.

Another object of the invention is the preparation of surface active compositions consisting of mixtures of alkyl oligosaccharides, alkyl glucosides and alkyl alcohols.

The alkyl oligosaccharides are highly effective surfactants for alkyl glucosides and mixtures of alkyl glucosides and alkyl alcohols. They are readily soluble in strongly alkaline solutions, thus facilitating the formulation of surface active materials in highly alkaline liquid systems. They, as well as mixtures thereof with alkyl glucosides and alkyl alcohols, also are useful as textile detergents, particularly in alkaline systems.

The prior art has known of alkyl oligosaccharides, but they have been of distinctly different structures from the compositions of the present invention, and their properties have been quite different, too. For example, Kato (Bull. Chem. Soc. Japan, 34, 718 (1961) (C.A. 56, 8832)) describes the preparation of alkyl maltosides by warming a solution of maltose in an aliphatic alcohol containing 0.1% HCl, the alcohols ranging from methyl to isooctyl. These maltosides are not surface active. Moreover, R ranges from C₃ to C₆, in contrast with the values for R in the present invention which range from C₁₂ to C₆. The value for m in these maltosides is 2, but unlike the critical requirement for the compositions of the present invention the value for m does not average at least 3.

Another example of the prior art is Hirai (Yakugaku Zasshi, 78, 999 (1955) (C.A., 53, 3073 (1959))) who describes the preparation of alkyl celluloses having alkyl groups in the range of C₃ to C₂₅. The value for m in these compounds is 2, but does not average at least 3 and thereby fails to meet the essential requirement of the present invention.

In U.S. Pat. 2,974,134 there is described the preparation of surface active alkyl ether glucosides and alkyl ether oligosaccharides by the reaction of oligosaccharides with an alkaline metal hydroxide to form an alkaline metal salt derivative which is then reacted with alkyl halides under pressure, followed by hydrolysis with a mineral acid to give a mixture of surface active ethers. These materials are ethers and not acetics as described in this application. The present compositions contain no ether links or semi-acetal groups; by contrast the materials of U.S. Pat. 2,974,134 contain both.

In U.S. Pat. 2,355,245 there is disclosed the preparation of polymers of alkyl glucosides by heating alkyl glucosides with an acid catalyst. In contrast with the compounds of the present invention, this reference discloses R as being a maximum of C₆ whereas in the present invention R is at least C₁₂, a critical factor to the high degree of surface activity and textile detergency which the product herein is capable of obtaining.

The process by which our novel alkyl oligosaccharide compositions, and our novel alkyl oligosaccharide-alkylalkylglucoside mixtures are prepared may generally be described as follows: a lower alkyl glucoside, preferably butyl glucoside, is prepared by a conventional Friedel-Crafts type reaction using from 1 to 12 mols of the lower alkyl per mol of glucoside. An acid catalyst is employed in the amount of from about 0.0005 mol per mol of glucose to about 0.05 mol/mole of glucose. The preferred catalyst is Fe₅O₇, although HCl, HNO₃, P-toluene sulfonic acid, methanesulfonic acid, and other acids, electron-accepting compounds of the group generally classed as "Lewis acids," may be employed. If sulfuric acid is employed as a catalyst it is preferred to use from 0.1 to 2.0 g./mol glucose (0.001 to 0.02 mol/mol glucose). If butanol or other lower alkyl alcohol is employed the preferred amount would be from 2 to 6 mols/mole glucose. The reaction is carried out at or above room temperature, preferably from 80 to 120° C., by refluxing until the mixture is clear and the glucose is in solution. Alternatively, the water of reaction may be removed during the reflux either by distillation with or without a reflux splitter or by azotropic separation using hexane, heptane, or other such azeotroping agents.

When conversion of the glucose to butyl glucoside has taken place, or when the reaction mixture is clear, the higher alcohol is added and the excess lower alkyl alcohol removed, the removal operation being facilitated by reducing the pressure in order to speed the distillation and keep the distillation temperature from getting too high. The amount of higher alcohol added generally will be from 0.5 to 4.0 mols/mol glucose, being dependent upon the final composition desired, the average molecular weight of the higher alkyl oligosaccharides which are formed being inversely proportional to the amount of the higher alcohol used. That is, oligomers with relatively high molecular weights are formed if the mol ratio of alcohol to glucose is relatively low, and vice versa.

When the higher alcohol has been added and the excess lower alcohol removed, an alcohol interchange reaction (trans-acetalation), already started, is continued by holding the reaction mixture at elevated temperatures under vacuum (if desired) so as continually to remove the lower alkyl as it and the higher alkyl glucosides and oligosaccharides are formed.

It should be understood that the components of the mixtures of alkyl oligosaccharides, alkyl glucosides and alkyl alcohols which can be prepared in accordance with the present invention may vary as follows. For each 100 parts by weight of the surface active mixture there may be present:

(a) From 0 to 50 parts of a compound having the structure ROH, where R is selected from the group consisting of aliphatic hydrocarbon radicals ranging from C₃H₇ to C₆H₁₄;

(b) From 10 to 70 parts of a glucoside having the structure ROG, where R is the same as in (a) above.
and where G is a glucosyl radical which is connected to the RO through its first carbon atom; and (c) From 20 to 90 parts of an alkyl oligosaccharide mixture whose components have the structure

$$R'OC(H_2O_2)_{m-1}H$$

where R' is selected from the group consisting of aliphatic hydrocarbon radicals ranging from $C_4H_{11}$ to $C_{26}H_{55}$ and m is at least 2 but averages at least 3.

It should be understood that components (a), (b) and (c) are present in fixed ratios to each other as stated. These values are not absolute, however, for there may be present inert materials, such as lower alkyl glucosides, which make up the balance of the composition.

The manner in which these ratios are varied is controlled by the amount of lower alcohol removed. The extent of reaction can be determined by a vapor phase chromatographic method of a sample at any time. The final composition of the product thus is a result of the amount of higher alcohol used but also the extent of the transacetalation reaction.

At some low mol ratios of the higher alcohol to glucose it may be desirable to terminate the interchange reaction even though appreciable amounts of butyl (or other lower alkyl) glycosides remain. This can insure a final product having a low alcohol content and consequently a lower viscosity and melting point than would be obtained if the interchange reaction were carried further. At higher mol ratios it is often desirable to continue the reaction further in order to obtain more "active" ingredient in the final product composition. Thus, the final composition may contain varying amounts of butyl glycosides which, although they do not contribute significantly to surface activity, in some cases they do insure desirable properties.

The relative amounts of the various components of the novel alcohol, alkyl glucoside and alkyl oligosaccharide compositions which are formed thus are determined by the mol ratio of alcohol/glucose and the extent of the transacetalation reaction. Thus, it is possible to control the nature of the end products of the invention so as to produce compositions with properties that are suitable for the intended use of the product. For example, increased higher alcohol content lowers the product's solubility in water and in alkaline solutions, but may cause an improvement in the solubility, or at least lower the viscosity of the product, so that it will be highly useful in a lubricating oil or cosmetic formulation. Materials with relatively high alkyl glucoside contents exhibit good textile detergency although they may not be as soluble as alka-line solutions or as good hydrotropes for other nonionic surfactants as those containing lower alkyl glucoside and more alkyl oligosaccharide.

In determining or controlling the properties of the product an important factor is the length of the hydrophobe in relation to the number of condensed glucoside units. Any variation in the structure of the product may have an effect on its hydrophilicity and hydrophobicity. Thus, it might be possible to prepare two different materials with properties which are similar in some respect. A mixture containing a relatively large amount of lauryl glucoside may have solubility properties that are similar to a mixture containing a relatively large amount of a dodecyl disaccharide.

If desired to separate out the novel alkyl oligosaccharide compositions from mixtures thereof along with alcohols and alkyl glucosides, this may be simply done by precipitating the alkyl oligosaccharides with a non-solvent such as acetone. The isolated oligosaccharides are useful as hydrotropes for alkyl glucosides and other surface active agents.

It is obvious, in the compositions described above, that to obtain a mixture of alkyl oligosaccharides in which the R group differs from that of the alkyl glucoside and alkanol, that the alkyl oligosaccharides would have to be isolated separately and then combined with the alkyl glucoside-alkanol mixture.

### Table I

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility</th>
<th>C, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauryl glucoside</td>
<td>Insoluble</td>
<td>0-10</td>
</tr>
<tr>
<td>De.</td>
<td>Water</td>
<td>0-10</td>
</tr>
<tr>
<td>De.</td>
<td>20% NaOH</td>
<td>0-100</td>
</tr>
<tr>
<td>Lauryl glucoside + (2 parts) and $C_6H_{12}$-conjugated oligosaccharide</td>
<td>Very slight haze</td>
<td>0-100</td>
</tr>
<tr>
<td>$C_6H_{12}$-conjugated oligosaccharide</td>
<td>Clear</td>
<td>0-10</td>
</tr>
<tr>
<td>Lauryl glucoside</td>
<td>Insoluble</td>
<td>0-10</td>
</tr>
<tr>
<td>De.</td>
<td>Water</td>
<td>Clear</td>
</tr>
<tr>
<td>De.</td>
<td>20% NaOH</td>
<td>Clear</td>
</tr>
<tr>
<td>Lauryl glucoside + (2 parts) and $C_6H_{12}$-conjugated oligosaccharide</td>
<td>Water</td>
<td>Clear</td>
</tr>
<tr>
<td>$C_6H_{12}$-conjugated oligosaccharide</td>
<td>20% NaOH</td>
<td>Clear</td>
</tr>
<tr>
<td>Lauryl glucoside + (2 parts) and $C_6H_{12}$-conjugated oligosaccharide</td>
<td>Water</td>
<td>Clear</td>
</tr>
<tr>
<td>$C_6H_{12}$-conjugated oligosaccharide</td>
<td>20% NaOH</td>
<td>Clear</td>
</tr>
<tr>
<td>De.</td>
<td>Water</td>
<td>0-100</td>
</tr>
<tr>
<td>De.</td>
<td>20% NaOH</td>
<td>0-100</td>
</tr>
<tr>
<td>Lauryl glucoside + (2 parts) and $C_6H_{12}$-conjugated oligosaccharide</td>
<td>Water</td>
<td>Clear</td>
</tr>
<tr>
<td>$C_6H_{12}$-conjugated oligosaccharide</td>
<td>20% NaOH</td>
<td>Clear</td>
</tr>
</tbody>
</table>

Lauryl glucoside was obtained as follows:
- A mixture of 40 parts of glucose, 222 parts of butanol, 6 parts of hexane and 1 part of concentrated sulfuric acid was stirred and refluxed for 15 hrs. at 100-105°C while the water of reaction was removed in an attached water separator. Then the mixture was then held for 4 hrs. at 80°C under vacuum while the butanol formed by the alcohol interchange reaction was removed. The mixture was neutralized with 8 parts of 50% sodium hydroxide solution.
- The reaction was then filtered from the product at 110°C, 20 mm Hg and the residue was washed once with 277 parts of acetone and then with three 177 parts portion of acetone. The combined acetone washings were distilled free of acetone to give a crude product which contained 10% of the alcohol of the alcohol.
- A mixture of 26 parts of this crude lauryl glucoside and 40 parts of a similar material obtained from another similar reaction, was further purified by vacuum distillation to remove unsaturated alcohol and washing with acetone to remove acetone insoluble oligosaccharides. The final dried product consisted of 24 parts and had the following analysis by vapor phase chromatography of the trimethylsilyl derivative:
  - Percent dodecyl glucoside: 80.0
  - Percent butyl glucoside: 6.5
  - Percent dodecyl alcohol: 36
  - Percent dodecyl oligosaccharide: 4.5

Glucose $C_6H_{12}$-conjugated oligosaccharide was obtained as follows:
- A mixture of 42.6 parts of a $C_6H_{12}$-conjugated alcohol-glucoside-oligosaccharide mixture (80% solids) and 40 ml. of ethanol was heated to 80°C and the mixture was filtered off and dried to 8.5 parts of a solid, acetone-insoluble $C_6H_{12}$-conjugated oligosaccharide.
- The sample of lauryl glucoside was obtained as follows:
  - The filtrate from the above experiment was stripped free of solvents to give 26.6 parts of an acetone insoluble material which is precipitated as a $C_6H_{12}$-conjugated glucoside.
- Lauryl glucoside prepared from dodecyl alcohol and glucose and purified in a manner similar to lauryl glucoside:
  - Analytical Percent dodecyl glucoside>95
  - Percent butyl glucoside>9
  - Percent dodecyl alcohol=2
  - Percent dodecyl oligosaccharide<0.3
- $C_6H_{12}$-conjugated oligosaccharide was obtained from a mixture with dodecyl alcohol and dodecyl glucoside by a procedure similar to that described for $C_6H_{12}$-conjugated oligosaccharide in a above.
In the preceding Table 1 the solubility in water and in aqueous sodium hydroxide of a series of compounds, including a number made in accordance with the present invention was evaluated at various temperatures. In each case one part of solute was added to 99 parts of solvent.

**EXAMPLE 1**

Preparation of lauryl glucoside-lauryl oligosaccharide-lauryl alcohol mixture

A mixture of 720 parts of glucose, 1779 parts of n-butanol, and 8 parts of concentrated sulfuric acid was stirred and refluxed at 100°-110° C. in a flask with an attached water separator using hexane to cause the water to separate in the trap. After the theoretical amount of water was collected (18 parts/180 parts glucose) there was added 2132 parts of lauryl alcohol and the excess butanol was removed by distillation. The alcohol interchange, in which the lauryl alcohol reacted with the butyl glycosides while the butanol of reaction was distilled from the flask, was followed by vapor phase chromatography of the trimethylsilyl derivatives. At completion of the interchange the reaction mixture was neutralized with sodium hydroxide solution. A 250 part portion of this was subjected to distillation up to a pot temperature of 145° C. at 10 mm. Hg. The distillate (lauryl alcohol) was 117 parts and the residue was 133 parts. A 10 part sample of the residue was removed for analysis and evaluation. The distillation was then continued to a pot temperature of 150° C. while another 22 parts of distillate was removed. The residual product of 98 parts of a lauryl alcohol, lauryl glucoside, lauryl oligosaccharide mixture was submitted for evaluation as a textile detergent and found by analysis to have the following composition:

**Percent**

Lauryl alcohol ......................................................... 20.5
Lauryl glucoside ..................................................... 41
Lauryl disaccharide ................................................... 14
Lauryl trisaccharide .................................................... 9
Lauryl tetrasaccharide .................................................. 7
Lauryl pentasaccharide ............................................... 5
Higher lauryl oligosaccharides ................................... 1.35

1 By difference.

**EXAMPLE 2**

Preparation of octadecyl oligosaccharide

A mixture of 180 parts of glucose, 444 parts of butanol, 40 parts of hexane and 2 parts of concentrated sulfuric acid was reacted in a flask with an attached water separator while the water of reaction was collected and butyl glycosides were formed. There was then added 540 parts of stearyl alcohol, and butanol was distilled out. The mixture was maintained at 100-105° C./4-5 mm. Hg, while the alcohol interchange reaction took place. The mixture was neutralized with 50% aqueous sodium hydroxide and the product was washed seven times with 3 liter portions of acetone. A total of 490 parts of acetone soluble material was obtained which was found by analysis (vapor phase chromatography of the trimethylsilyl derivative) to be a mixture of stearyl alcohol and stearyl glucoside. The acetone insoluble portion of 137 parts was shown by similar analysis to contain only a small amount of stearyl alcohol and no stearyl glucoside; 97.2% solids, 44.86% carbon and 7.22% hydrogen. The theoretical elemental analysis for an octadecyl oligosaccharide containing an average of 12.5 condensed saccharide units is 48.5% carbon and 7.22% hydrogen. A 35 part sample of this octadecyl oligosaccharide and 300 parts of 0.5 N hydrochloric acid was stirred and refluxed for 20 hours and then hydrogenated 5 times with 200 ml. portions of hexane. Distillation of the hexane extracts yielded 4.1 g. of recovered octadecan. This corresponds to the amount expected by hydrolysis of an octadecyl oligosaccharide having an average of 12.5 condensed saccharide units.

**EXAMPLE 3**

Preparation of butyl carbityl oligosaccharides and butyl carbityl glucoside

A mixture of 180 parts of glucose, 648 parts of butoxyethoxyethanol ("butyl Carbitol"), about 15 parts of hexane and 2 parts of concentrated sulfuric acid was stirred and refluxed at 105° C. for 6 hours while 21.0 parts of water was removed in a water separator. A solid precipitated during the reaction. The mixture was neutralized and filtered. The residue was washed twice with toluene and dried to 101 parts of a tan powder. Vapor phase chromatography of the trimethylsilyl derivative showed the absence of butyl carbityl glucoside and butyl Carbitol. The solid (butyl carbityl oligosaccharides) was insoluble in acetone. The combined filtrate and toluene washes were distilled free of solvents and butyl Carbitol to 127 parts of material which was predominately butyl carbityl glucoside.

**EXAMPLE 4**

Preparation of a mixture of alcohols, alkyl glucosides and alkyl oligosaccharides in which the alkyl group of each component is a mixture of C_{15}H_{31} and C_{15}H_{33}

A mixture of 90 parts of glucose, 111 parts of butanol, about 4 parts of hexane and 0.25 part of concentrated sulfuric acid was stirred and refluxed while 10 parts of water was collected in a water separator. There was added 127 parts of a mixture of alkanols comprised predominantly of about equal parts of n-dodecanol and n-tridecanol. The mixture was held at 100-110° C./10 millimeters of mercury while butanol was removed by distillation and the alcohol interchange reaction was taking place. The mixture was then neutralized with 5 parts of 50% sodium hydroxide solution. It was diluted with 150 parts of heptane and a practically clear solution resulted. A sample was removed for evaluation as a surfactant in gasoline.

**EXAMPLE 4a**

Preparation of a mixture of octadecyl alcohol, octadecyl glucoside and octadecyl oligosaccharides

A mixture of octadecyl alcohol, octadecyl glucoside and octadecyl oligosaccharide prepared in a similar manner from 90 parts of glucose, 224 parts of butanol, 6 parts of hexane, 2 parts of sulfuric acid and 405 parts of octadecanol, from which some excess octadecanol had been removed by distillation (yield 308 parts), was evaluated for solubility in oils. It was clear at the levels of 0.5% and 2.0% in mineral seal oil and in a high aromatic oil. A clear solution for analysis as a corrosion inhibitor in motor oils was obtained by mixing 10 parts of the product with 90 parts of a S.A.E. 10 motor oil.

Analysis of the product showed that it contained 15% octadecanol, 25% octadecyl glucoside and 60% octadecyl oligosaccharides, each percentage being by weight.

**EXAMPLE 5**

Preparation of a mixture of a quaternary ammonium cationic surface active agent and an alkyl glucoside-alkyl oligosaccharide-alkanom mixture

A mixture of 3.2 parts of a 50% active aqueous solution of a quaternary ammonium cationic surface active agent, and 6.4 parts of an alkyl glucoside, alkyl oligosaccharide and alkanol mixture, in which the alkyl radicals were predominantly a mixture of n-C_{15}H_{31} and n-C_{15}H_{33} alkyl groups, was dissolved in 80 parts of water to give a clear solution with a pH of 10.2. A fabric treated with this mixture was shown to have antibacterial properties.

**EXAMPLE 6**

Preparation of various mixtures of alkanols, alkyl glucosides and alkyl oligosaccharides

The general procedure, already described, for synthesizing a mixture of alkanols, alkyl glucosides, and alkyl
oligosaccharides from glucose and a higher alcohol via a butyl glycoside intermediate was used to prepare a variety of products. The alcohol used in these experiments was commercially available mixture comprised predominantly of dodecyl and tetradecyl alcohols, leading to the formation of C_{12}H_{25} and C_{14}H_{29} alkanols, alkyl glycosides and alkyl oligosaccharides. Various mol ratios of alcohol/glucose were used, the products were analyzed by vapor phase chromatography of the trimethylsilyl derivatives, and the results are shown in Table II below:

### Table II

<table>
<thead>
<tr>
<th>Percent</th>
<th>Alkyl group</th>
<th>Oligosaccharides with more than 2 condensed glycoside units</th>
</tr>
</thead>
<tbody>
<tr>
<td>82</td>
<td>C_{6}H_{12}</td>
<td>--------------------------------------------------------</td>
</tr>
<tr>
<td>95</td>
<td>C_{12}H_{25}</td>
<td>---------------------------------------------------------</td>
</tr>
<tr>
<td>&gt;95</td>
<td>C_{16}H_{37}</td>
<td>---------------------------------------------------------</td>
</tr>
</tbody>
</table>

We claim:

1. A mixture consisting essentially of alkyl oligosaccharides, alkyl glycosides and alkanols, the surface active ingredients of which mixture, for each 100 parts by weight present, consists of:
   (a) from 0 to 50 parts of a compound having the structure ROH, where R is a member of the group consisting of alliphatic hydrocarbon radicals ranging from C_{12}H_{25} to C_{14}H_{29};
   (b) from 10 to 70 parts of a glucose having the structure ROG, where R is the same as in (a) above, and where G is a glycosyl radical which is connected through its number one carbon atom to RO; and
   (c) from 20 to 90 parts of an alkyl oligosaccharide mixture whose components have a structure of the formula
     \[ R'O(C_{6}H_{12}O_{2})_{n}H \]
     where R' is a member of the group consisting of alliphatic hydrocarbon radicals ranging from C_{12}H_{25} to C_{16}H_{37}, the radical (C_{6}H_{12}O_{2}) represents a glycosyl unit, m is at least 2 but averages at least 3, and one of the glycosyl units is connected through its number one carbon to RO.

2. The mixture of claim 1 in which both R and R' are C_{6}H_{12}.
3. The mixture of claim 1 in which both R and R' are C_{12}H_{25}.
4. The mixture of claim 1 in which both R and R' are C_{14}H_{29}.
5. The mixture of claim 1 in which both R and R' are C_{16}H_{37}.
6. The mixture of claim 1 in which ROH is a mixture of H_{2}C_{6}H_{4}OH and H_{2}C_{14}H_{29}OH, ROG is a mixture of H_{2}C_{6}H_{4}OG and H_{2}C_{14}H_{29}OG, and R'O(C_{6}H_{12}O_{2})_{n}H is a mixture of H_{2}C_{6}H_{4}O(C_{6}H_{12}O_{2})_{m}H and H_{2}C_{14}H_{29}O(C_{6}H_{12}O_{2})_{m}H.

7. The mixture of claim 1 in which ROH is a mixture of H_{2}C_{6}H_{4}OH, H_{2}C_{12}H_{25}OH, H_{2}C_{14}H_{29}OH and H_{2}C_{16}H_{37}OH; ROG is a mixture of H_{2}C_{6}H_{4}OG, H_{2}C_{12}H_{25}OG, H_{2}C_{14}H_{29}OG and H_{2}C_{16}H_{37}OG; and R'O(C_{6}H_{12}O_{2})_{n}H is a mixture of H_{2}C_{6}H_{4}O(C_{6}H_{12}O_{2})_{m}H, H_{2}C_{12}H_{25}O(C_{6}H_{12}O_{2})_{m}H, H_{2}C_{14}H_{29}O(C_{6}H_{12}O_{2})_{m}H, and H_{2}C_{16}H_{37}O(C_{6}H_{12}O_{2})_{m}H.

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  - 2,258,168 10/1941 White

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- U.S. Cl. X.R.
  - 252—158; 260—209, 210