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TOBACCO INCORPORATING CARBONATE ESTERS OF FLAVORANTS

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This invention relates to novel carbonate esters of flavorants, and to their usage for the purpose of controlling the release of the flavorant. More particularly, this invention relates to these novel carbonate esters of flavorants, and to their use in tobacco products for the purpose of incorporating the desired flavorant in such form that it will not be released during the subsequent processing and storage but which will be released in the desired amount upon smoking to impart improved aroma, flavor and taste effects.

The use of flavoring additives in tobacco products has become of increased importance in the tobacco industry due to the lowered aromaticity of the available tobacco and to the increased preference of some smokers for filter cigarettes. The addition of certain desirable flavorants to tobacco is limited by their volatility which causes them to be lost or diminished in quantity during processing and storage of the tobacco product. This problem is even more acute for filter cigarettes containing active adsorbents, such as charcoal, in the filters. During the processing and storage of this type of product, volatile flavorants migrate from the tobacco and are irreversibly bound by the active adsorbent, thereby depleting the flavorant in the product and possibly altering the effectiveness of the active adsorbent in its selective removal of undesirable smoke components.

Menthol is a flavorant which has received high acceptance as an additive to tobacco products because of the pleasant cooling effect and desirable aroma and flavor characteristics which it imparts to the smoke. Its high degree of volatility and ease of sublimation have presented problems in the manufacturing operations and, in addition, have resulted in a decreased shelf-life of the product due to losses of menthol by diffusion on storage. Activated adsorbents, such as charcoal, in the filters of mentholated cigarettes possess a high affinity for menthol and cause its depletion from the tobacco at an excessive rate thereby decreasing the amount available to the smoker to below an acceptable level after a relatively short time of storage.

It is therefore an object of this invention to provide novel carbonate esters which are synthesized from a flavorant alcohol, which may be incorporated into a smoking article and which upon smoking will release the flavorant into the smoke.

It is another object of this invention to provide such novel carbonate esters which may be incorporated into the tobacco of the smoking article and which will not migrate from the tobacco during processing or storage of the finished article but will release the flavorant into the smoke at a controlled rate during the smoking process.

It is a further object of this invention to provide novel smoking articles containing these carbonate esters.

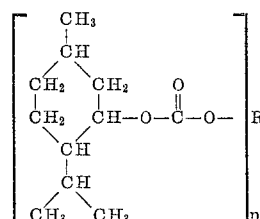
It is a still further objective of this invention to provide filter cigarettes containing an active adsorbent in the filter and novel carbonate esters in the tobacco which bind a flavorant in non-volatile form and release it during the smoking process.

Therefore, according to this invention, there are provided novel carbonate esters which are sufficiently stable and non-volatile under the conditions of their storage environment and which decompose appropriately under smoking conditions to release the flavorant into the smoke.

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A preferred class of these carbonate esters are mixed carbonate esters of menthol and a polyhydroxy compound, of which the polyhydroxy compound portion of the molecule may be derived from monosaccharides such as pentoses and hexoses of which xylose and glucose are representative members; disaccharides of which sucrose is a representative member; trisaccharides of which raffinose is a representative member; polysaccharides of which starch, cellulose and guar gum are representative members; or glycols, of which glycerin and propylene glycol are representative members.

The general formula for this preferred class of mixed carbonate esters of menthol and a polyhydroxy compound is as follows:



where the magnitude of n depends on the nature of R, and R is a polyhydroxy compound selected from the group consisting of monosaccharides, disaccharides, trisaccharides, polysaccharides and glycols.

These compounds may be prepared by any of several methods. One such method involves the reaction of menthol with carbonyl chloride (phosgene) to form menthyl chloroformate. The chloroformate is then allowed to react with the hydroxylated compound in an appropriate solvent to give the desired carbonate ester. For example, the synthesis of O-(menthoxycarbonyl) glucose compounds involves the reaction of the desired amount of menthyl chloroformate with glucose in a solvent such as pyridine. One to four moles of menthyl chloroformate per glucose molecule may be employed to give this formation of mono-, di-, tri-, or tetra-O-(menthoxycarbonyl) glucose respectively. A limiting factor is the over-saturation of the carbohydrate molecule with menthoxycarbonyl groups in which event a portion of the menthol may eliminate in such a way as to give rise to menthene, which in excessive amounts may be in turn detrimental to the aroma and flavor of the smoking composition.

Specific examples of the preparation of menthyl carbonates of polyhydroxy compounds that may be used as flavoring additives for tobacco products are as follows:

EXAMPLE 1

Mono-O-(menthoxycarbonyl) glucose

Into a 5-l., three-neck flask immersed in a Dry-Ice-acetone bath at -75°C . is introduced 1176 gms. (12 moles) of liquid phosgene. A sample of 1301 gm. (8.35 moles) of menthol, dissolved in one liter of cyclopentane, is added to the phosgene over a period of one hour, while the solution is being stirred. The reaction flask is then allowed to reach room temperature and the phosgene allowed to reflux for six hours. At the end of this period the excess phosgene, cyclopentane and the hydrogen chloride formed during the reaction is removed under reduced pressure. The crude menthyl chloroformate (about 2 liters) is mixed with 500 ml. of ether and the solution washed once with one liter of an aqueous solution containing 110 gm. of sodium bicarbonate, and twice with one liter portions of distilled water. The organic layer is dried over anhydrous sodium sulfate and the solvent evaporated at reduced pressure.

The menthyl chloroformate is divided into eight equal aliquots. Each aliquot, containing one mole of the menthyl chloroformate, is added, over a period of one hour,

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to a solution of 180 gm. (1 mole) d-glucose in 2.5 liters of pyridine cooled in an ice bath. The reaction mixture is then allowed to reach room temperature and is stirred for an additional 4 hours. The pyridine is removed under vacuum.

The residual thick liquid is poured into a mixture of 300 ml. of concentrated hydrochloric acid in 300 gm. of ice. To this is added 500 ml. of ether to aid in the solution of the gelatinous precipitate. The organic layer is re-extracted two more times with 500-ml. portions of ether. The combined ether extracts are washed three times with 250-ml. portions of 4 N hydrochloric acid, once with 200 ml. of water, once with 100 ml. of saturated sodium bicarbonate solution, and again with 200 ml. of water. The organic layer is then decolorized with charcoal, dried over anhydrous sodium sulfate, and the ether is evaporated under vacuum.

The product from eight batches was combined to give 2463 gm. of a white solid softening at 69° C. This represents 81% of the theoretical yield based on menthol.

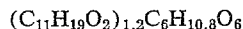
The product, when measured in CCl_4 solution, had infrared absorption bands at 1750 and 1265 cm^{-1} , characteristic of the $\text{C}=\text{O}$ and $\text{C}-\text{O}$ stretching vibrations observed for acyclic carbonates of saturated alcohols of this type (J. L. Hales, J. T. Jones and W. Kynaston, J. Chem. Soc., 618 (1957); B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *ibid.*, 3130 (1958)), and exhibited bands at 1385 and 1394 cm^{-1} characteristic of the isopropyl group present in menthol.

The number of O-menthoxy carbonyl groups per molecule was calculated on the basis of the molar extinction for the $\text{C}=\text{O}$ stretching band observed at 1750 cm^{-1} as follows:

Infrared spectro in the 2 to 15 μ region were recorded for the O-menthoxy carbonyl compounds in CCl_4 solution at concentrations of 6 g./liter using a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics and 0.05 cm. path length cells. An average value for the apparent carbonyl extinction per $\text{C}=\text{O}$ group was obtained by measurement of the values at 1750 cm^{-1} for di-, tri- and tetra-O-(menthoxy carbonyl) glucose. The relative number of O-menthoxy carbonyl groups per molecule was then estimated by dividing the total extinction found for an individual compound by the average extinction per $\text{C}=\text{O}$ group.

Estimates of the relative number of O-menthoxy carbonyl groups per molecule calculated from extinction measurements of the methyl $\text{C}-\text{H}$ stretching band at 2960 cm^{-1} were found to agree well with the estimates based on the $\text{C}=\text{O}$ extinctions. Also, the apparent molecular extinction coefficients for the $\text{O}-\text{H}$ stretching frequency at 3500 cm^{-1} were observed to vary inversely with the number of O-menthoxy carbonyl groups in the molecule, as expected.

It was found that 1.2 moles of O-menthoxy carbonyl groups had been incorporated, on an average, into 1.0 mole of glucose. Elemental analysis gave: C, 57.20%, 57.38%; H, 8.84%, 8.71%. Calculated for



C, 57.8%; H, 8.5%.

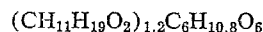
Analysis for methyl groups was carried out by measurement of the intensity of the characteristic absorption at 5917 cm^{-1} as follows:

Analyses for methyl groups were performed with a Perkin-Elmer Model 350 spectrophotometer using concentrations of approximately 1% in CCl_4 and silica cells of 1 cm. path. Molecular extinction coefficients were measured for the first overtone absorption of the asymmetric methyl $\text{C}-\text{H}$ stretching band at 5917 cm^{-1} . The number of methyl groups per mole was determined by comparing the measured molecular extinction values to the average molecular extinction of absorbance per mole of methyl group which was determined by the analysis

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of a large number of known compounds of varied structure.

Found: 4.1 CH_3 . Calculated for



5 3.6 CH_3 .

The menthol content, determined by vapor phase chromatography following saponification with alcoholic NaOH, was found to be 41%. Pyrolysis at 250° C. yielded 39% menthol. The theoretical menthol content based on an average formula of $(\text{C}_{11}\text{H}_{19}\text{O}_2)_{1.2}\text{C}_6\text{H}_{10.8}\text{O}_6$ is 47.6%.

EXAMPLE 2

Di-O-(menthoxy carbonyl) glucose

Twenty-two grams (0.1 mole) of menthyl chloroformate is added dropwise to an ice-cooled solution of 9 gm. (0.05 mole) d-glucose in 150 ml. of pyridine. The addition is completed in one hour, after which time the temperature of the reaction mixture is raised to 25° C. After partial evaporation of the pyridine, the reaction mixture is poured into a beaker containing 30 ml. concentrated hydrochloric acid and 50 gm. of ice. Following thorough mixing, the composite is extracted three times with equal volumes of ether. The combined ether extracts are washed with three 25-ml. portions of 4 N hydrochloric acid; one 25-ml. portion of water followed by 25 ml. of a saturated sodium bicarbonate solution and one 25-ml. portion of water. The organic layer is dried over anhydrous sodium sulfate and the ether is removed under vacuum. The semicrystalline product is stripped of residual solvent by drying under high vacuum, yielding 25.9 gm. of di-O-(menthoxy carbonyl) glucose, a white solid softening at 67° C. This represents 95% of the theoretical yield based on menthol.

The product, when measured in CCl_4 solution, had infrared absorption bands at 1751 and 1263 cm^{-1} , characteristic of the $\text{C}=\text{O}$ and $\text{C}-\text{O}$ stretching vibrations observed for acyclic carbonates of saturated alcohols of this type, and exhibited bands at 1385 and 1394 cm^{-1} characteristic of the isopropyl group present in menthol.

The number of O-menthoxy carbonyl groups per molecule was calculated on the basis of the molar extinction for the $\text{C}=\text{O}$ stretching band observed at 1751 cm^{-1} using the method as set forth in Example 1. It was found that 2.0 moles of O-menthoxy carbonyl groups had been incorporated, on an average, into 1.0 mole of glucose. Elemental analysis gave: C, 61.36%, 61.46%; H, 8.98%, 9.16%. Calculated for $(\text{C}_{11}\text{H}_{19}\text{O}_2)_2\text{C}_6\text{H}_{10}\text{O}_6$: C, 61.74%; H, 8.88%.

Analysis for methyl groups was carried out by measurement of the intensity of the characteristic absorption at 5917 cm^{-1} using the method set forth in Example 1.

Found: 6.5 CH_3 . Calculated for $(\text{C}_{11}\text{H}_{19}\text{O}_2)_2\text{C}_6\text{H}_{10}\text{O}_6$: 6.0 CH_3 .

The menthol content, determined by vapor phase chromatography following saponification with alcoholic NaOH, was found to be 57%. Pyrolysis at 250° C. yielded 35% menthol. The theoretical menthol content of di-O-(menthoxy carbonyl) glucose is 57.4%.

EXAMPLE 3

Tri-O-(menthoxy carbonyl) glucose

In a 500-ml. round-bottom flask is placed 6 gm. (0.033 mole) of anhydrous d-glucose and 150 ml. of pyridine. After the sugar has dissolved, the flask and contents are cooled in an ice-bath. To the cool solution is added 21.8 gm. (0.1 mole) of menthyl chloroformate over a period of one hour, with stirring. The reaction is allowed to proceed for an additional two hours and then is brought to ambient temperature. The mixture is then made acidic with concentrated hydrochloric acid and extracted with ether several times. The combined ether extract is decolorized with charcoal and dried over anhydrous sodium sulfate. The solvent is then removed at reduced pres-

sure, depositing 17 gms. of a white solid, tri-O-(menthoxy-carbonyl) glucose, melting at 65° C.

The product, when measured in CCl₄ solution, had infrared absorption bands at 1755 and 1261 cm.⁻¹, characteristic of the C=O and C—O stretching vibrations observed for acyclic carbonates of saturated alcohols of this type, and exhibited bands at 1385 and 1394 cm.⁻¹ characteristic of the isopropyl group present in menthol.

The number of O-menthoxycarbonyl groups per molecule was calculated on the basis of the molar extinction for the C=O stretching band observed at 1755 cm.⁻¹ using the method set forth in Example 1. It was found that 3.0 moles of O-menthoxycarbonyl groups had been incorporated, on an average, into 1.0 mole of glucose. Elemental analysis gave: C, 64.64%, 64.71%; H, 9.24%, 9.21%. Calculated for (C₁₁H₁₉O₂)_{3.0}C₆H₉O₆: C, 64.43%, H, 9.15%.

Analysis for methyl groups was carried out by measurement of the intensity of the characteristic absorption at 5917 cm.⁻¹ using the method set forth in Example 1.

Found: 8.7 CH₃. Calculated for (C₁₁H₁₉O₂)_{3.0}C₆H₉O₆: 9.0 CH₃.

The menthol content, determined by vapor phase chromatography following saponification with alcoholic NaOH, was found to be 63%. The theoretical menthol content of the tri-O-(menthoxycarbonyl) glucose is 64.5%.

EXAMPLE 4

Tetra-O-(menthoxycarbonyl) glucose

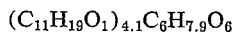
In a 500-ml. round-bottom flask is placed 7.2 gm. (0.04 mole) of anhydrous d-glucose and 300 ml. of pyridine. After the sugar has dissolved, the flask and contents are cooled in an ice-bath. To the cool solution is added 35 gm. (0.16 mole) of menthyl chloroformate over a period of one hour, with stirring, during which time the reaction mixture is held at 0° to 10° C. The reaction is allowed to reach ambient temperature and stirring continued for an additional five hours. The excess pyridine is then removed under reduced pressure. To the residue is added a mixture of 100 gm. of ice, 100 ml. of concentrated hydrochloric acid and 1 l. of ether. The ether is removed and the aqueous layer is extracted two more times with equal volumes of ether. The combined ether extracts are washed with three 150-ml. portions of 3 N hydrochloric acid, one 100-ml. portion of 10% aqueous sodium bicarbonate, and two 100-ml. portions of water. The ether solution is dried over anhydrous sodium sulfate and after filtration, the solvent is removed under vacuum. The semi-crystalline product is stripped of residual solvent by drying under vacuum; yielding 27.18 gm. of tetra-O-(menthoxycarbonyl) glucose, a white solid softening at 63–65° C. A yield of 75% of the theoretical, based on menthol, was obtained.

The product, when measured in CCl₄ solution, had infrared absorption bands at 1759 and 1259 cm.⁻¹, characteristic of the C=O and C—O stretching vibrations observed for acyclic carbonates of saturated alcohols of this type, and exhibited bands at 1385 and 1394 cm.⁻¹ characteristic of the isopropyl group present in menthol.

The number of O-menthoxycarbonyl groups per molecule was calculated on the basis of the molar extinction for the C=O stretching band observed at 1759 cm.⁻¹ using the method set forth in Example 1. It was found that 4.1 moles of O-menthoxycarbonyl groups had been incorporated, on an average, into 1.0 mole of glucose. Elemental analysis gave: C, 65.94%, 66.13%; H, 9.19%, 9.26%. Calculated for (C₁₁H₁₉O₂)_{4.1}C₆H₉O₆: C, 66.17%; H, 9.33%.

Analysis for methyl groups was carried out by measurement of the intensity of the characteristic absorption at 5917 cm.⁻¹ using the method set forth in Example 1.

Found: 12.3 CH₃. Calculated for



12.3 CH₃.

The menthol content, determined by vapor phase chromatography following saponification with alcoholic NaOH, was found to be 66%. The theoretical menthol content based on an average formula of (C₁₁H₁₉O₂)_{4.1}C₆H₉O₆ is 69%.

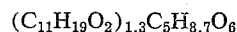
EXAMPLE 5

Mono-O-(menthoxycarbonyl) xylose

In a reaction flask is placed 24 gm. (0.16 mole) of xylose and 500 ml. of pyridine. The flask and contents are cooled to 0° C. To the cold solution is added with stirring 35 gm. (0.16 mole) of menthyl chloroformate over a period of two hours. The reaction mixture is then warmed to room temperature and the excess pyridine is removed under reduced pressure. The residue is mixed with 100 gm. of ice, 100 ml. of concentrated hydrochloric acid and 500 ml. of ether. The ether layer is removed and the aqueous solution is extracted twice more with equal volumes of ether. The ether extracts are combined and backwashed in the same manner as set forth in Example 2. Subsequently the ether is evaporated under vacuum depositing 21.5 gm. of the white solid, mono-O-(menthoxycarbonyl) xylose, melting at 121° C.

The product, when measured in CCl₄ solution, had infrared absorption bands at 1750 and 1267 cm.⁻¹, characteristic of the C=O and C—O stretching vibrations observed for acyclic carbonates of saturated alcohols of this type, and exhibited bands at 1385 and 1394 cm.⁻¹ characteristic of the isopropyl group present in menthol. Elemental analysis gave: C, 59.69%, 59.37%; H, 8.55%, 8.74%. This data is in agreement with an average molecular formula of (C₁₁H₁₉O₂)_{1.3}C₅H_{8.7}O₅: C, 59.58%; H, 8.71%.

The menthol content, determined by vapor phase chromatography following saponification with alcoholic NaOH, was found to be 48%. The theoretical menthol content based on an average formula of



is 52.5%.

EXAMPLE 6

Penta-O-(menthoxycarbonyl) sucrose

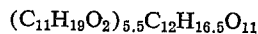
To 300 ml. of pyridine is added 17.1 gm. (0.05 mole) of sucrose (dried in vacuo at 70° C. overnight). Only partial solution of the sugar is obtained. Subsequently the flask containing the mixture is cooled to .5° C. and to the cool solution is added with stirring 21.8 gm. (0.1 mole) of menthyl chloroformate over a period of 2 hours. The reaction mixture is then allowed to reach room temperature and to stir overnight. After appropriate work up in a manner similar to that described in Example 2 above, there is obtained a white solid, penta-O-(menthoxycarbonyl) sucrose, melting at 65° C.

The product, when measured in CCl₄ solution, had infrared absorption bands at 1755 and 1263 cm.⁻¹, characteristic of the C=O and C—O stretching vibrations observed for acyclic carbonates of saturated alcohols of this type, and exhibited bands at 1385 and 1394 cm.⁻¹, characteristic of the isopropyl group present in menthol.

The number of O-menthoxycarbonyl groups per molecule was calculated on the basis of the molar extinction for the C=O stretching band observed at 1755 cm.⁻¹ using the method set forth in Example 1. It was found that 5.5 moles of O-menthoxycarbonyl groups had been incorporated, on an average, into 1.0 mole of sucrose. Elemental analysis gave: C, 64.59%, 64.53%; H, 9.26%, 9.05%. Calculated for (C₁₁H₁₉O₂)_{5.5}C₁₂H_{16.5}O₁₁: C, 64.75%; H, 9.07%.

Analysis for methyl groups was carried out by measurement of the intensity of the characteristic absorption at 5917 cm.⁻¹ using the method set forth in Example 1.

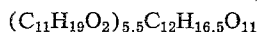
Found: 17.8 CH₃. Calculated for



75 16.5 CH₃.

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The menthol content, determined by vapor phase chromatography following saponification with alcoholic NaOH, was found to be 58.0%. The theoretical menthol content based on an average formula of



is 64%.

EXAMPLE 7

Tetra-O-(menthoxy carbonyl) raffinose

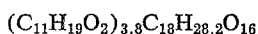
A sample of raffinose pentahydrate is dehydrated by heating at 85° C. under reduced pressure of 2 mm. for 6.5 hours. Approximately 23 gm. (0.045 mole) of the dry raffinose is dissolved in 100 ml. of pyridine. The solution is cooled to 10° C. and to it is added with stirring 30 gm. (0.137 mole) of menthyl chloroformate over a period of 1 hour. The mixture is then brought to room temperature and allowed to remain overnight. The pyridine is removed at reduced pressure. The residue is mixed with 100 gm. of ice, 100 ml. of concentrated hydrochloric acid and 500 ml. of ether. The ether layer is removed and the aqueous solution is extracted twice more with equal volumes of ether. The ether extracts are combined and backwashed in the same manner as set forth in Example 2. Subsequently the ether is evaporated under vacuum depositing 17.5 gm. of the white solid, tetra-O-(menthoxy carbonyl) raffinose, melting at 99° C.

The product, when measured in CCl₄ solution, had infrared absorption bands at 1750 and 1262 cm.⁻¹, characteristic of the C=O and C—O stretching vibrations observed for acyclic carbonates of saturated alcohols of this type, and exhibited bands at 1385 and 1394 cm.⁻¹ characteristic of the isopropyl group present in menthol.

The number of O-menthoxy carbonyl groups per molecule was calculated on the basis of the molar extinction for the C=O stretching band observed at 1750 cm.⁻¹ using the method set forth in Example 1. It was found that 3.8 moles of O-menthoxy carbonyl groups had been incorporated, on an average, into 1 mole of raffinose. Elemental analysis gave: C, 60.21%, 59.95%; H, 8.49%, 8.90%. Calculated for (C₁₁H₁₉O₂)_{3.8}C₁₈H_{28.2}O₁₆: C, 59.96%; H, 8.52 %.

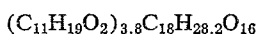
Analysis for methyl groups was carried out by measurement of the intensity of the characteristic absorption at 5917 cm.⁻¹ using the method set forth in Example 1.

Found: 11.3 CH₃. Calculated for



11.4 CH₃.

The menthol content, determined by vapor phase chromatography following saponification with alcoholic NaOH, was found to be 47.3%. The theoretical menthol content based on an average formula of



is 49.5%.

EXAMPLE 8

Mono-O-(menthoxy carbonyl) propane-1,2-diol

To a solution of 2.6 gm. (0.033 mole) 1,2-propanediol and 2.7 gm. (0.034 mole) pyridine in 100 ml. of ether, maintained at 0–5° C, is added with stirring 7.3 gm. (0.033 mole) of menthyl chloroformate over a period of one hour. The reaction mixture is brought to ambient temperature and stirring continued for an additional 40 minutes. The reaction mixture is then allowed to stand for two more days. The precipitate formed is collected on a filter and discarded. The filtrate is washed successively with three 15-ml. portions of 3 N hydrochloric acid, one 15-ml. portion of 10% aqueous sodium bicarbonate and two 15-ml. portions of water. The ether is removed at reduced pressure to leave 3.94 gm. of liquid mono-O-(menthoxy carbonyl) propane-1,2-diol.

The product, when measured in CCl₄ solution, had infrared absorption bands at 1752 and 1266 cm.⁻¹, characteristic of the C=O and C—O stretching vibrations observed for acyclic carbonates of saturated alcohols of

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this type, and exhibited bands at 1385 and 1394 cm.⁻¹, characteristic of the isopropyl group present in menthol. Elemental analysis gave: C, 65.23%, 64.93%; H, 9.81%, 10.04%. Calculated for (C₁₁H₁₉O₂)C₃H₈O₂: C, 65.08%, H, 10.15%.

Analysis for methyl groups was carried out by measurement of the intensity of the characteristic absorption at 5917 cm.⁻¹ using the method set forth in Example 1.

Found: 3.7 CH₃. Calculated for (C₁₁H₁₉O₂)C₃H₈O₂ 4.0 CH₃.

The menthol content, determined by vapor phase chromatography following saponification with alcoholic NaOH, was found to be 60%. Pyrolysis at 250° C. yielded 16% menthol. The theoretical menthol content of mono-O-(menthoxy carbonyl) propane-1,2-diol is 61%.

EXAMPLE 9

Mono-O-(menthoxy carbonyl) glycerol

A sample of glycerol is dried by heating in an open dish to a temperature of 185° C. for 2 hours. Approximately 14.7 gm. (0.16 mole) of the dry glycerol is dissolved in 500 ml. of pyridine. The solution is cooled to 5° C. and to it is added with stirring 35 gm. (0.16 mole) of menthyl chloroformate over a period of 45 minutes. The mixture is then brought to room temperature and allowed to remain overnight. The pyridine is removed at reduced pressure. The residue is mixed with a cold solution of 100 ml. of water and 100 ml. of concentrated hydrochloric acid. This is then extracted three times with equal volumes of ether. The ether extracts are washed in the same manner as described in Example 2. The solvent is evaporated under vacuum yielding 7.0 gm. of the liquid mono-O-(menthoxy carbonyl) glycerol.

The product, when measured in CCl₄ solution, had infrared absorption bands at 1750 and 1267 cm.⁻¹, characteristic of the C=O and C—O stretching vibrations observed for acyclic carbonates of saturated alcohols of this type, and exhibited bands at 1385 and 1394 cm.⁻¹, characteristic of the isopropyl group present in menthol. Elemental analysis gave: C, 62.06%, 62.18%; H, 9.43%, 9.55%. Calculated for (C₁₁H₁₉O₂)C₃H₇O₃: C, 61.29%; H, 9.55%.

The menthol content, determined by vapor phase chromatography following saponification with alcoholic NaOH, was found to be 56%. The theoretical menthol content of mono-O-(menthoxy carbonyl) glycerol is 57%.

The examples set forth above are for illustrative purposes only and do not limit our invention to the compounds listed. Compounds of menthoxy carbonyl and any polyhydroxy compound, which release menthol upon smoking as previously described, may be used.

The proportion of O-(menthoxy carbonyl) polyhydroxy compound that may be incorporated in a tobacco product may be widely varied in accordance with taste and to achieve the desired cooling effect. It may also be used in conjunction with varying amounts of free menthol if desired.

However, we have found that desirable cooling effects are obtained when the content of the O-(menthoxy carbonyl) polyhydroxy compound is such that the menthol equivalent is between 0.01 and 1.0% by weight of the smoking tobacco product.

In practicing our invention, we have found that any convenient method may be used to incorporate these menthyl compounds in the smoking tobacco product. Thus, the menthyl compound may be dissolved in a suitable solvent and may be applied to the cured, cased and blended tobacco by spraying or dipping. Also the menthyl compound may be applied to the paper or leaf wrapper by spraying, dipping or brushing or any other method in general use in the industry. Further, the menthyl compound may be dissolved or suspended in all or a portion of the casing solution and applied to the cured, and blended tobacco by spraying or dipping. Still another mode of application may be by incorporating the menthyl com-

pound into the homogenized ground tobacco components prior to reconstituting into a sheet.

Specific examples of incorporating O-(menthoxy carbonyl) polyhydroxy compounds into a tobacco product are as follows:

EXAMPLE 10

A mixture composed of approximately 1.4 grams of di-O-(menthoxy carbonyl) glucose and 0.3 gram of 1-menthol was dissolved in 4 ml. of 95% ethanol. The solution was applied by spraying to 200 gms. of a commercial blend of cased and cut tobacco in a rotating glass drum. The solvent was evaporated and the treated tobacco manufactured into cigarettes on a Chico-type cigarette making machine.

EXAMPLE 11

Approximately 3.2 grams of tri-O-(menthoxy carbonyl) glucose was dissolved in 6 ml. of 95% ethanol. The solution was applied by spraying to 200 grams of a commercial blend of cased and cut tobacco. After evaporation of the ethanol, the treated tobacco was manufactured into cigarettes on a Chico-type cigarette making machine.

EXAMPLE 12

A sample of approximately 2.6 grams of tetra-O-(menthoxy carbonyl) glucose was dissolved in 6 ml. of petroleum ether. The solution was applied by spraying to 200 grams of a commercial blend of cased and cut tobacco. The solvent was removed completely and the treated tobacco was manufactured into cigarettes on a Chico-type cigarette making machine.

EXAMPLE 13

Approximately 2.8 grams of mono-O-(menthoxy carbonyl) glucose was dissolved in 4 ml. of 95% ethanol. The solution was then applied by spraying with an atomizer to 200 grams of a commercial blend of cased and cut tobacco in a rotating drum. The ethanol was allowed to evaporate from the tobacco. The treated tobacco was manufactured into cigarettes on a Chico-type cigarette making machine.

EXAMPLE 14

Approximately 5 pounds of mono-O-(menthoxy carbonyl) glucose was dissolved in 26 pounds of a casing solution containing in certain proportions, amounts of invert sugar, corn syrup and humectants normally used to case tobaccos destined for the manufacture of cigarettes. The solution was heated to 170° F. and was maintained at that temperature for two and one-half hours. Subsequently the casing solution was applied to 150 pounds of a commercial blend of tobacco strip. The treated tobacco strip was mixed with other tobacco components in sufficient amounts to give 230 pounds of finished product at the proper moisture level. This product was processed through all of the manufacturing operations required to give a cased and cut, finished tobacco blend. This blend was then manufactured into cigarettes, fitted with three-piece charcoal filters, in a regular production, high speed cigarette making machine.

EXAMPLE 15

Approximately 44.7 gm. of mono-O-(menthoxy carbonyl) glucose was suspended in a solution of 169.0 ml. of glycol humectants and 1500 ml. of water. This mixture was added to 2240 gms. of a ground tobacco composition containing in certain proportions cellulose fibers and a water-soluble binder. After thorough mixing the wet composition was manufactured into a coherent tobacco sheet. The total weight of sheet at the appropriate moisture level was approximately 2400 gm. Menthol analysis of the finished product following alkaline hydrolysis, indicated that the theoretical level of 7.9 mg. of menthol per gram of product was achieved.

Approximately 42 pounds of product, prepared by repeating the above procedure several times, was mixed with 150 pounds of a commercial blend tobacco strip which had been cased with 30.19 pounds of a special casing solution containing 3.29 pounds of mono-O-(menthoxy carbonyl) glucose, and 57.1 pounds of other tobacco components. After appropriate blending, cutting, and drying operations the blend was manufactured into cigarettes by a high speed cigarette making machine. To the cigarettes were subsequently attached three-piece charcoal filters.

EXAMPLE 16

Approximately 3.1 pounds of mono-O-(menthoxy carbonyl) glucose was dissolved in 29.1 pounds of a casing solution containing in certain proportions, amounts of invert sugar, corn syrup and humectants normally used to case tobacco destined for the manufacture of cigarettes. The solution was heated to 17° F. and was maintained at that temperature for two hours. Subsequently the casing solution was applied to 219 pounds of a commercial blend of tobacco strip. The treated tobacco strip was mixed with other tobacco components in sufficient amounts to give 283 pounds of finished product at the proper moisture level. This product was processed through all of the manufacturing operations required to give a cased and cut, finished tobacco blend. This blend was then treated with a solution containing approximately 0.55 pound of free 1-menthol and smaller amounts of other flavorants. The treated blend was then manufactured into cigarettes, fitted with three-piece charcoal filters, in a regular production, high speed cigarette making machine.

EXAMPLE 17

Approximately 2.0 gm. of mono-O-(menthoxy carbonyl) propane-1,2-diol was applied, by spraying in ethanolic solution, to 200 gm. of a commercial blend cased and cut tobacco. After evaporation of the ethanol, the treated tobacco was manufactured into cigarettes in a Chico-type cigarette making machine.

EXAMPLE 18

A sample of 0.640 gm. of mono-O-(menthoxy carbonyl) xylose was dissolved in enough ethanol to give a final volume of solution of 1 ml. Aliquots of 20 μ l. of the solution were injected, uniformly along a path of 55 mm. length, in commercially available cigarettes equipped with charcoal filters. The solvent was removed from each cigarette by a gentle stream of air.

EXAMPLE 19

A sample of 0.535 gm. of mono-O-(menthoxy carbonyl) glycerol was dissolved in enough ethanol to give a final volume of solution of 1 ml. Aliquots of 20 μ l. of the solution were injected, uniformly along a path of 55 mm. length, in commercially available cigarettes equipped with charcoal filters. The solvent was removed from each cigarette by a gentle stream of air.

EXAMPLE 20

Approximately 0.680 gm. of penta-O-(menthoxy carbonyl) sucrose was dissolved in enough ethanol to give a final volume of solution of 2.5 ml. Aliquots of 50 μ l. of the solution were injected, uniformly along a path of 55 mm. length, in commercially available cigarettes equipped with charcoal filters. The solvent was removed from each cigarette by a gentle stream of air.

EXAMPLE 21

A sample of approximately 0.670 gm. of tetra-O-(menthoxy carbonyl) raffinose was dissolved in enough ethanol to give a final volume of solution of 2.5 ml. Aliquots of 50 μ l. of the solution were injected uniformly along a path of 55 mm. length, in commercially available cigarettes

equipped with charcoal filters. The solvent was removed from each cigarette by a gentle stream of air.

Samples of the cigarettes, prepared as described in the examples cited above, and equipped with charcoal filters of the type disclosed in the Keith et al. copending application Ser. No. 262,653, filed on Mar. 4, 1963, were selected to be representative on the basis of firmness and equivalent pressure drop. These cigarettes were then smoked, the smoke characteristics evaluated by an experienced taste panel, and the amount of menthol in the smoke analyzed. The menthol analysis involved the vapor phase chromatography of pyridine-ethanol solutions of the smoke utilizing a Perkin-Elmer Model 154D vapor fractometer equipped with a H₂ flame ionization detector. A 0.25 inch OD x 9 ft. copper column containing 30-60 mesh Chromosorb W coated with 10% Castorwax MP-80 was used for the separation. The column was maintained at 152° C., and helium at a flow rate of 190 cc./min. was used as the carrier gas. The method was calibrated with solutions of menthol of known concentrations. A relative standard deviation of about 3% was observed for the method. The results of these tests are summarized in Table I below:

TABLE I.—SUMMARY OF RESULTS ON CIGARETTES CONTAINING O-(MENTHOXYCARBONYL) POLYHYDROXY COMPOUNDS

Example No.	Compound added to tobacco	Calculated level of menthol equivalent ¹ mg./cig.	Menthol Analysis, mg./puff	Flavor Evaluation ²	
				Taste	Cooling
10.....	Di-O-(menthoxy carbonyl): Glucose.....	4.5	0.040	1.5	2
	Free menthol.....	1.6			
11.....	Tri-O-(menthoxy carbonyl): Glucose.....	7.3	0.055	2.5	3
	Free menthol.....	1.4			
12.....	Tetra-O-(menthoxy carbonyl): Glucose.....	6.2	0.021	T	T
	Free menthol.....	1.1			
13.....	Mono-O-(menthoxy carbonyl): Glucose.....	5.0	0.060	3	3
	Free menthol.....	2.1			
14.....	Mono-O-(menthoxy carbonyl): Glucose.....	5.8	0.057	3	3
	Free menthol.....	0.0			
15.....	Mono-O-(menthoxy carbonyl): Glucose.....	6.1	0.030	3	2.5
	Free menthol.....	0.0			
16.....	Mono-O-(menthoxy carbonyl): Glucose.....	3.4	0.048	3	3
	Free menthol.....	1.5			
17.....	Mono-O-(menthoxy carbonyl) propane-1,2-diol.....	5.3	0.0125	½	T
18.....	Mono-O-(menthoxy carbonyl) xylose.....	5.4	0.0311	1	2
19.....	Mono-O-(menthoxy carbonyl) glycerol.....	5.3	0.0142	T	T
20.....	Penta-O-(menthoxy carbonyl) sucrose.....	7.0	0.0147	½	½
21.....	Tetra-O-(menthoxy carbonyl) raffinose.....	5.5	0.0281	½	1½

¹ Menthol equivalents is based on the yield obtained on base hydrolysis after correction for free menthol content of the preparations.

² O=No menthol. T=Threshold menthol. 1=Low menthol. 2=Medium menthol. 3=High menthol.

All of the samples were judged to confer the cooling characteristic of menthol to the smoke. Cigarettes prepared as described in Example 10 and fitted with charcoal filters produced a smoke with a moderate level of menthol taste and exhibited good smoothness. The menthol effect was unique in its persistent after-cooling effect. Sample cigarettes prepared as described in Example 11 produced a smoke having moderate to high level of menthol cooling and had a taste with an unusual residual after-cooling effect and overall good balance. Cigarettes prepared as described in Example 12 produced a smoke having a threshold level of menthol and a bitter taste associated with menthene. The menthene was probably produced by menthol elimination which might be expected due to the over-saturation of the glucose with menthoxy carbonyl groups. Cigarettes prepared as described in Example 13 produced a smoke having a moderately high level of menthol taste and cooling. Cigarettes prepared as described in Example 14 as well as in Example 15 exhibited a satisfying level of menthol cooling and taste which is quite persistent throughout the cigarette. The menthol impression is particularly notable

on the tongue as it produces a spice-like stimulation. The cooling impression is noticed on the inhaling as well as on exhaling. Cigarettes prepared as described in Example 16 exhibited a well balanced smoke flavor profile. They produced a moderate level of menthol cooling on the first puff. The menthol impression persists uniformly throughout the cigarette. These cigarettes produce a unique "clean-ness" especially in the aftertaste.

Cigarettes prepared as described in Example 17 produced a smoke having a threshold level of menthol cooling and flavor. Cooling decreased while menthol flavor increased toward the end of the cigarette. Cigarettes prepared as described in Example 18 produced a smoke having a moderate level of menthol cooling impact and a low menthol flavor which increased slightly during smoking. Cigarettes prepared as described in Example 19 produced a smoke having a threshold level of menthol cooling and taste which diminished to sub-threshold level toward the end of the cigarette. Cigarettes prepared as described in Example 20 produced a smoke having a trace to low initial menthol impression which increased slightly toward the end of the cigarette. These cigarettes produced a persistent residual cooling effect. Cigarettes pre-

pared as described in Example 21 produced a smoke having a moderate menthol cooling impression with a woody taste.

These cigarettes present a distinct and unusual flavor effect to the smoker. On inhalation, the smoke produces a gentle cooling effect on the mouth and throat. On exhaling, the smoker perceives a spice-like cooling and taste effect which lingers in the mouth and throat as a clean, comfortable aftertaste.

Studies of the migration rate of menthol in cigarettes containing active adsorbents, such as charcoal, in the filters, illustrate the superiority of the compositions of this invention over conventional menthol application. Comparative studies were carried out with cigarettes prepared as described in Example 14 and a control sample, 14-Q. The control, 14-Q, contained free menthol sprayed on the tobacco blend prior to the manufacture of the cigarettes. It will be appreciated that both samples contained activated charcoal filters of the same type. The cigarettes were permitted to age independently at two temperature levels, 75° F. and 100° F. At various time intervals during aging, cigarettes of the sample and control

were analyzed for menthol content in the tobacco plus paper and in the charcoal of the filters. The extent of migration of the menthol to the charcoal was thus obtained from the menthol analyses. The results of these studies are shown in Table II below.

TABLE II.—MENTHOL MIGRATION STUDIES

Aging temperature, ° F.	Cigarette age in days	Percent menthol migrating from the tobacco to the charcoal filter	
		Cigarettes treated only with free menthol 14-Q	Cigarettes treated with mono-O-(menthoxy-carbonyl) glucose, Example 14
75-----	0	0	0
	14	33	0.9
	31	42	
	84	65	4
100-----	0	0	0
	7	40	2
	14	57	4
	21	66	5
	28	72	7
	84	-----	12

As can be seen, the conventionally mentholated cigarette, sample 14-Q, had a high rate of menthol migration even at 75° F. with the rate of migration increased substantially at 100° F. The sample cigarette prepared as described in Example 14 and containing one of the compounds of this invention gave only slight menthol migration, even at 100° F.

Analysis of representative components of the gas phase of smoke from cigarettes prepared as described in Example 14, indicated no difference either in composition or quantities when compared to those of a comparative control sample.

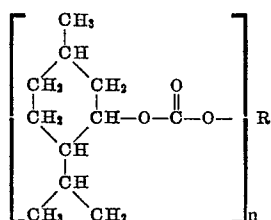
It will also be appreciated that the filtration efficiency of the activated charcoal in the filter of cigarettes containing the preparations of this invention will not be diminished by migrating menthol.

It will thus be seen that the compounds of this invention can be applied in several ways to tobacco, will survive the normal cigarette processing operation, will not be significantly lost from the tobacco on storage for an extended period and will provide adequate menthol impression in the cigarette smoke.

Having thus provided a written description of the present invention and provided specific examples thereof, it should be understood that no undue restrictions or limitations are to be imposed by reason thereof, but that the present invention is defined by the appended claims.

What is claimed is:

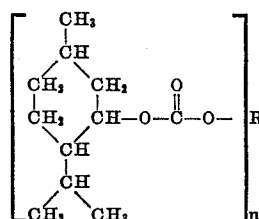
1. A smoking article comprising tobacco and having incorporated in said tobacco a minor proportion of a compound which decomposes upon ignition of said tobacco thereby releasing free menthol into the smoke stream, said compound having the general formula:



wherein the magnitude of n depends on the nature of R, and R is a polyhydroxy compound selected from the

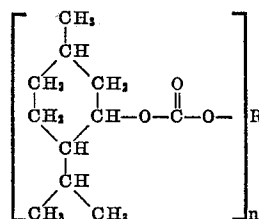
group consisting of monosaccharides, disaccharides, trisaccharides, polysaccharides and glycols.

2. An activated charcoal filtered smoking article comprising tobacco and having incorporated in said tobacco a minor proportion of a compound which decomposes upon ignition of said tobacco thereby releasing free menthol into the smoke stream, said compound having the general formula:



wherein the magnitude of n depends on the nature of R, and R is a polyhydroxy compound selected from the group consisting of monosaccharides, disaccharides, trisaccharides, polysaccharides and glycols.

3. A method of producing a smoking article having an activated charcoal filter and adapted to release a mentholated smoke which comprises incorporating in the tobacco of said smoking article a minor proportion of a compound having the general formula:



wherein the magnitude of n depends on the nature of R, and R is a polyhydroxy compounds selected from the group consisting of monosaccharides, disaccharides, trisaccharides, polysaccharides and glycols, whereby upon ignition of said tobacco, said compound is decomposed thereby releasing free menthol into the smoke stream.

4. A smoking article according to claim 1 wherein said polyhydroxy compound is selected from the group consisting of monosaccharides, disaccharides and trisaccharides.

5. A smoking article according to claim 1 wherein said polyhydroxy compound is a polysaccharide.

6. A smoking article according to claim 1 wherein said polyhydroxy compound is a glycol.

7. A smoking article comprising tobacco and having incorporated in said tobacco a minor proportion of the compound mono-O-(menthoxy-carbonyl) glucose which decomposes upon ignition of the tobacco, thereby releasing free menthol into the smoke stream.

8. A smoking article comprising tobacco and having incorporated in said tobacco a minor proportion of the compound di-O-(menthoxy-carbonyl) glucose which decomposes upon ignition of the tobacco, thereby releasing free menthol into the smoke stream.

9. A smoking article comprising tobacco and having incorporated in said tobacco a minor proportion of the compound mono-O-(menthoxy-carbonyl) xylose which decomposes upon ignition of the tobacco, thereby releasing free menthol into the smoke stream.

15

10. A smoking article comprising tobacco and having incorporated in said tobacco a minor proportion of the compound penta-O-(menthoxycarbonyl) sucrose which decomposes upon ignition of the tobacco, thereby releasing free menthol into the smoke stream.

11. A smoking article comprising tobacco and having incorporated in said tobacco a minor proportion of the compound tetra-O-(menthoxycarbonyl) raffinose which decomposes upon ignition of the tobacco, thereby releasing free menthol into the smoke stream.

5

10

16

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SAMUEL KOREN, *Primary Examiner*.

MELVIN D. REIN, *Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,332,428

July 25, 1967

James D. Mold et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

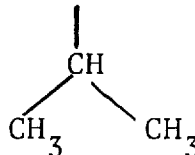
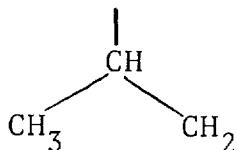
Column 1, line 22, for "increased" read -- increasing --; column 2, line 39, for "this" read -- the --; column 4, line 4, for the left-hand portion of the formula reading

$$(\text{CH}_{11} \quad \text{read} \quad \text{C}_{11})$$

column 6, line 38, for the right-hand portion of the formula reading

$$0_6 \quad \text{read} \quad 0_5$$

column 7, line 75, for "carbona tes" read -- carbonates --;
column 10, line 19, for "17°" read -- 170° --; columns 11
and 12, Table I, heading to the sixth column, for "Coolling"
read -- Cooling --; column 13, lines 63 to 73, for that portion
of the formula reading



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column 14, line 30, for "minnor" read -- minor --; line 47,
for "compounds" read -- compound --.
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Signed and sealed this 9th day of July 1968.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents