

UNITED STATES PATENT OFFICE

2,483,099

ESTERS OF POLYHYDROXY-BENZOIC ACIDS

Steward G. Morris, Philadelphia, and Roy W. Riemenschneider, Glenside, Pa., assignors to the United States of America as represented by the Secretary of Agriculture

No Drawing. Application June 21, 1946,
Serial No. 678,188

11 Claims. (Cl. 260—473)

(Granted under the act of March 3, 1883, as
amended April 30, 1928; 370 O. G. 757)

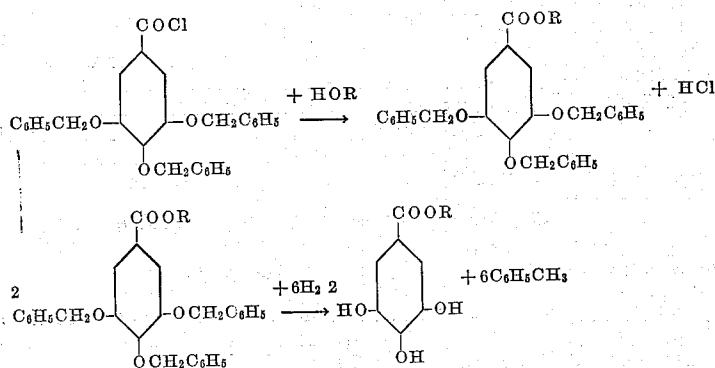
1

This application is made under the act of March 3, 1883, as amended by the act of April 30, 1928, and the invention herein described, if patented, may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment to us of any royalty thereon.

This invention relates to esters of polyhydroxy-benzoic acids, more particularly to the higher alkyl esters of gallic acid and has for its object the production of these esters.

Gallic acid esters of the lower fatty alcohols can be obtained by direct esterification in the presence of catalysts such as concentrated sulfuric acid or anhydrous hydrogen chloride. When this procedure is used in an attempt to bring about esterification of gallic acid with higher aliphatic alcohols containing more than six carbon atoms in the molecule the corresponding esters are not formed or the reaction yields only a very small amount of impure products.

We have found that alkyl esters of gallic acid containing six or more carbon atoms in the alkyl radical can be obtained by the following procedure. Gallic acid is converted to galloyl-chloride tribenzyl-ether which is reacted with an aliphatic alcohol containing six or more carbon atoms per molecule to form the corresponding tribenzyl-gallic acid ester, which on hydrogenation yields the gallic acid alkyl ester as shown by the following equations:



We prefer to convert gallic acid to galloyl chloride tribenzyl-ether by first preparing methyl gallate, benzylating it to obtain the methyl ester of tribenzyl gallic acid, saponifying the ester group to form gallic acid tribenzyl ether and converting this compound to galloyl chloride tribenzyl ether by treating it with thionyl chloride. Galloyl

2

chloride tribenzyl ether can be obtained by other methods, for instance, by benzylation of gallic acid to form the benzyl ester of tribenzyl gallic acid, followed by saponification of the ester group and subsequent conversion of the carboxyl group to acyl-chloride group by means of phosphorus penta-chloride, thionyl chloride, or sulfuryl chloride.

Debenzylation of tribenzyl gallic acid esters of higher aliphatic alcohols is best effected by hydrogenation in the presence of hydrogenation catalysts such as for example palladium, platinum, or nickel which may be used in conjunction with a carrier such as for instance charcoal.

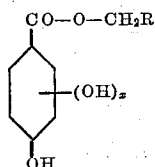
Our invention is applicable to the production of the higher alkyl esters of gallic acid from the higher aliphatic alcohols of the olefine series. The alkylene esters of tribenzyl gallic acid obtained by reacting galloyl chloride tribenzyl ether with these unsaturated alcohols when subjected to catalytic hydrogenation are hydrogenated at the double bonds of the alkylene radicals and at the same time debenzylated yielding the corresponding alkyl esters of gallic acid.

We have found that our invention is also applicable to the production of long chain alkyl esters of other polyhydroxybenzoic acids such as for example protocatechuic acid. Alkyl esters of polyhydroxybenzoic acid containing at least six carbon atoms in the alkyl radical are useful as in-

intermediates in the production of other compounds. They are more readily soluble in oily and fatty substances than the corresponding esters of lower aliphatic alcohols, and are useful as antioxidants for fatty materials as disclosed in our application for Patent Serial No. 685,633 filed July 23, 1946.

3

Among our new products are those of the following formula:



in which $\text{—CH}_2\text{R}$ is an alkyl hydrocarbon radical having a straight chain of at least seven carbon atoms, x being an integer not exceeding two. In a preferred group the straight chain has at least twelve carbon atoms.

The invention is further characterized as including n -alkyl esters of gallic acid containing at least seven carbon atoms, and preferably at least twelve carbon atoms, in the alkyl radical.

As illustrative embodiments of a manner in which our invention may be carried out in practice the following examples are given.

Example I

A solution obtained by heating 250 grams of commercial gallic acid (containing one molecule of crystallization water) with 750 cc. methyl alcohol, is saturated with hydrogen chloride at 0°C . and allowed to stand overnight at this temperature. Approximately 400 cc. of the solvent are then distilled off and on cooling the distillation residue to 0°C . methyl gallate is obtained as a crystalline precipitate.

Fifty-nine grams of the methyl gallate so obtained are dissolved in 250 cc. of anhydrous acetophenone, 142 grams of dry powdered potassium carbonate are added to the solution, which is then heated at 140°C . while 130 grams of benzyl chloride are added dropwise and with agitation over a period of $1\frac{1}{2}$ hours. After stirring the mixture for seven hours at $140\text{--}150^\circ\text{C}$. the acetophenone is removed by steam distillation, the distillation residue is extracted with benzene and methyl ester of tribenzyl gallic acid contained in the extract is crystallized from benzene-petroleum ether.

Fifty-five grams of tribenzyl gallic acid methyl ester are heated under reflux, for about 30 minutes, with 10 grams of potassium hydroxide dissolved in 20 cc. of water, and 350 cc. ethyl alcohol. The solution thus obtained is poured into 1500 cc. of cold water containing 20 cc. of concentrated hydrochloric acid. The precipitate consisting of gallic acid tribenzyl ether is filtered off and crystallized from absolute alcohol-benzene mixture. The product so obtained has a melting point of 195°C . The yield is 49 grams.

Example II

A mixture of 49 grams gallic acid tribenzyl ether and 135 cc. thionyl chloride is heated first at 50°C . for about 30 minutes, then the temperature is raised to 60°C . over a period of approximately $1\frac{1}{2}$ hours. Excess thionyl chloride is then distilled off at the water pump while maintaining the temperature at 60°C . To remove traces of thionyl chloride the distillation residue is dissolved in benzene and again evaporated to dryness. The galloyl chloride tribenzyl ether thus obtained is crystallized from benzene-petroleum ether. The yield is 46.5 grams of galloyl chloride tribenzyl ether melting at 116.5°C .

Example III

Ten grams of galloyl chloride tribenzyl ether prepared as described in Example II, and 8.12

4

grams of lauryl alcohol are melted at 120°C . and the mixture is heated at 90°C . for approximately one hour. The lauryl ester of tribenzylgallic acid thus obtained is crystallized from petroleum ether (boiling range $30\text{--}70^\circ\text{C}$.). The yield is 12.9 grams of a product melting at $71.5\text{--}72^\circ\text{C}$.

Example IV

Eleven and twenty-five hundredths grams lauryl ester of tribenzyl gallic acid prepared as described in Example III and a hydrogenation catalyst prepared by reducing 1 gram palladium chloride on 6 grams of charcoal, as described by Ott and Schroeter (1927 Ber. 60, 633), are added to approximately 150 cc. of absolute alcohol. The mixture is heated to dissolve the ester, and is then hydrogenated under approximately 45 pounds hydrogen pressure. The reaction is usually completed within five to ten minutes. The solution is filtered to remove the catalyst and evaporated to dryness on a water bath and under reduced pressure. The lauryl gallate thus obtained consists essentially of n -dodecyl ester of gallic acid which on crystallization from petroleum ether-benzene solvent has a melting point of $96.5\text{--}97^\circ\text{C}$.

Example V

By following the procedure described in Example IV and replacing the lauryl alcohol used in that example by the equimolecular amount of any one of the following alcohols:

n -Hexyl alcohol
 n -Octyl alcohol
 n -Tetradecyl alcohol (myristyl alcohol)
 n -Hexadecyl alcohol (cetyl alcohol)
 n -Octadecyl alcohol (stearyl alcohol)

the corresponding alkyl esters of tribenzyl-gallic acid are obtained,

	Melting point, $^\circ\text{C}$.
n -Hexyl ester	72-73
n -Octyl ester	74.5
n -Tetradecyl ester	75.5-76
n -Hexadecyl ester	79.5-80
n -Octadecyl ester	83.5-84

Example VI

Debenzylation by catalytic hydrogenation as described in Example IV using instead of lauryl ester of tribenzyl-gallic acid, the equimolecular amount of any one of the alkyl esters described in Example V yields the corresponding esters of gallic acid.

	Melting point, $^\circ\text{C}$.
n -Hexyl gallate	93.5
n -Octyl gallate	94-95.7
n -Tetradecyl gallate	98.5-99.2
n -Hexadecyl gallate	99.5-100
n -Octadecyl gallate	104.5

Hydrogenation may be conducted at 35-45 pounds pressure.

Example VII

Six and nine-tenths grams of oleyl alcohol are added to 9.1 grams of galloyl chloride tribenzyl ether prepared as described in Example II. The mixture is heated at 120°C . for 3 hours and the product thus obtained consisting essentially of oleyl alcohol-ester of tribenzyl gallic acid on crystallization from petroleum ether melts at 39°C .

The oleyl alcohol ester of tribenzyl gallic acid thus obtained is dissolved in 150 cc. of warm ethyl alcohol, and hydrogenated in the presence of 0.3 gram of platinum catalyst prepared as

described in Gilman and Blatt's "Organic Syntheses" (Collective volume I, second ed. 1941, page 463), at about 42 pounds hydrogen pressure. On completion of the hydrogenation the solution was filtered, and the solvent evaporated. The residue crystallized from benzene-petroleum ether has a melting point of 103.5-104.2° C. and consists of octadecyl gallate.

Analogous results are obtained using other hydrogenation catalysts such as palladium on charcoal.

Having thus described our invention, we claim:

1. The process of producing an alkyl ester of an acid of the group consisting of gallic acid and protocatechuic acid which comprises reacting a compound of the group consisting of galloyl chloride tribenzyl ether and protocatechuic acid chloride-dibenzyl ether with a primary monohydric alcohol and de-benzylating by subjecting the resulting ester to catalytic dehydrogenation.

2. The process of producing alkyl esters of gallic acid containing at least six carbon atoms in the alkyl radical which comprises reacting galloyl chloride tribenzyl ether with a primary aliphatic alcohol containing at least six carbon atoms per molecule, to form the tribenzyl gallic acid ester of said alcohol and then de-benzylating without de-esterifying by subjecting said ester to catalytic hydrogenation.

3. The process as defined in claim 2 wherein the primary aliphatic alcohol is a saturated alcohol.

4. The process as defined in claim 2 wherein the primary aliphatic alcohol is a saturated alcohol containing from 6 to 18 carbon atoms per molecule.

5. The process of producing n-dodecyl ester of gallic acid which comprises reacting galloyl chloride tribenzyl ether with n-dodecyl alcohol to form the n-dodecyl ester of tribenzyl gallic acid and then de-benzylating without de-esterifying by subjecting said ester to catalytic hydrogenation.

6. The process of producing n-tetradecyl ester of gallic acid which comprises reacting galloyl chloride tribenzyl ether with n-tetradecyl alcohol

to form the n-tetradecyl ester of tribenzyl gallic acid and then de-benzylating without de-esterifying by subjecting said ester to catalytic hydrogenation.

7. The process of producing n-octadecyl ester of gallic acid which comprises reacting galloyl chloride tribenzyl ether with n-octadecyl alcohol to form the n-octadecyl ester of tribenzyl gallic acid and then debenzylating without de-esterifying by subjecting said ester to catalytic hydrogenation.

8. The process as defined in claim 2 in which the primary aliphatic alcohol is a monohydric alcohol.

9. The process described in claim 2 in which the catalytic hydrogenation is with hydrogen gas under pressure in the presence of palladium-charcoal catalyst.

10. The process described in claim 5 in which the catalytic hydrogenation is with hydrogen gas under pressure in the presence of palladium-charcoal catalyst.

11. The process described in claim 10 in which the hydrogenation is in absolute alcohol.

STEWART G. MORRIS.

ROY W. RIEMENSCHNEIDER.

REFERENCES CITED

The following references are of record in the file of this patent:

- Hepner et al., "Chem. Abstracts," vol. 27 (1933), p. 280.
 Staudinger et al., "Chem. Abstracts," vol. 32 (1938), p. 766.
 Suter et al., JACS, vol. 61, February 1939, p. 531.
 Cavallito et al., "Jour. Am. Chem. Soc.," vol. 65 (1943), pp. 2140-2142.
 Bergel, Chemistry and Industry, page 127-128, Apr. 1, 1944 (Abridged from paper read before a meeting of the Food Group of the Society on Oct. 13, 1943).
 Bucher, "Fisher Market News," vol. 7 (1945), No. 7 (July) pp. 18 and 19.
 McKenzie et al., "Jour. Chem. Soc." (London) vol. 95, p. 548.