CITRIC ACID ESTERS

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3 Claims. (Cl. 260--484)

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This application is a continuation in part of
the copending applications, S. N. 608,101, filed
July 31, 1945; S. N. 608,102, filed July 31, 1945;
S. N. 608,380, filed August 1, 1945, and S. N.
747,848, filed May 13, 1947.

This invention relates to citric acid esters and
more particularly to mono- and di-esters of citric
acid.

An object of this invention is to provide agents
which retard for relatively prolonged periods the
development of rancidity in glyceridic oils, and in
certain glyceridic oils retard the development of
the so-called flavor reversion.

Another object of this invention is to provide
agents which affect marked moisture retention
characteristics in glyceridic oil compositions such
as margarine.

Another object of this invention is to provide
agents by means of which other agents, which
per se are relatively insoluble or immiscible in
glyceridic oils, are incorporated in such oils.

In the copending applications, S. N. 608,101,
now Patent No. 2,485,631, S. N. 608,102, now Paten-
t No. 2,485,632, and S. N. 608,380, now Patent
No. 2,485,633, comparative tests are described
which demonstrate that certain monoesters when
incorporated in glyceridic oils markedly retard
deterioration of such oils. For example, mono-
esteryl citrate when incorporated in corn salad
oil is capable of retarding materially the develop-
ment of rancidity of the oil as indicated by peroxy-
idic number determinations. On the other hand,
certain diesters of citric acid incorporated in mar-
garine materially improve the moisture retention
characteristics as described in the copending ap-
plication S. N. 747,848, now Patent No. 2,485,634,
while certain di- and tri-citric acid esters facil-
itate the incorporation of the monoesters in gly-
ceridic oils as described for example in the co-
pending application S. N. 608,102.

The mono- and di-esters of citric acid of this
invention are new compounds and may be em-
ployed as ingredients in the compositions dis-
closed and claimed in these copending applica-
tions. The citric acid esters of this invention
have the following formula:

\[ RC_\text{Citric Acid} \]

in which \( Z \) is a member of the class consisting of
hydrogen and monovalent hydrocarbon radicals
having the formula:

\[ R_1 R_2 \]

\[ R_3 = \text{C--C--} \]

\[ R_4 \]

in which, in the formula 1 above and in the hy-
drocarbon radicals (2) above, \( R_1, R_2, R_3 \) and \( R_4 \)
are members selected from the class consisting of
hydrogen and monovalent hydrocarbon substitu-
ts, such as alkyl or alkylen substituents, at least
one of the members \( R_1, R_2, R_3 \) and \( R_4 \) being
a hydrocarbon substituent, and when the ester is
a monoalkyl citrate and one of the members \( R_1,
R_2 \) and \( R_3 \) is an isopropyl group, the number of
carbon atoms in the ester is at least 12. If the
ester of citric acid be a diester, the two hydro-
carbon radicals in the formula 1 above may be
the same or different. For example, one may be
a palmitoyl and the other a stearoyl radical to
constitute palmitoyl stearoyl citrate, or again one may
be a stearoyl radical and the other an oleoyl radical
to constitute oleoyl stearoyl citrate. Such diesters
result from the reaction of mixed alcohols, such as
a mixture of oleoyl alcohol and oleoyl alcohol
with citric acid as described in Example 5 of the
copending application S. N. 747,846.

The hydrocarbon radicals may be connected
through an ester linkage to one or both terminal
carbonyl groups of the citric acid nucleus in ac-
cordance with the following formula:

\[ H \]

\[ H-C-O-O-\]

\[ H \]

in which \( X \) and \( X_1 \) are members of the class con-
sisting of hydrogen and monovalent hydrocarbon
radicals having the formula:

\[ R_5 \]

\[ R_6 \]

\[ R_7 \]

\[ R_8 \]

in which \( R_1, R_2, R_3 \) and \( R_4 \) are members selected
from the class consisting of hydrogen and mono-
valent hydrocarbon substituents, such as alkyl.
or alkylene substituents, at least one of the members R1, R2, R3 and R4 being a hydrocarbon substituent, and when the ester is a monoalkyl citrate and one of the members R1, R2 and R4 is an alkyl propyl group, the number of carbon atoms in the hydrocarbon radical is at least 6. At least one of the members X and Xi is an organic radical. In the diesters, X and Xi may be the same such as in di(propyl) citrate or different such as in di(octyl) stearyl citrate. In addition to the esters represented by the Formula 3 above, this invention also embraces esters in which a hydrocarbon radical is connected through an ester linkage to the carbon atom of the central carbonyl group of the citric acid nucleus.

As discussed in the copending application S. N. 747,848, dialkyl or dialkylene esters of citric acid, in which the alkyl or alkylene group has at least 8 carbon atoms and more particularly in which the alkyl group has at least 12 carbon atoms or in which the alkylene group has at least 16 carbon atoms are especially effective for preventing the exudation of milk moisture from margarine. The esters of this invention are prepared by reacting citric acid with an alcohol having the following formula:

$$R_1\quad R_2\quad R_3\quad R_4$$

in which R1, R2, R3 and R4 have the same meaning as herebefore defined. Preferably, the citric acid and the alcohol are reacted in proportions which favor the formation of the mono- or di-ester of citric acid which is desired. As described in the copending applications, it is frequently desired to utilize a mixture of the mono- and di-esters rather than employ the monoester or diester alone. For that purpose, the proportion of the citric acid and alcohol may be regulated to obtain the desired ratio of mono-, di- and tri-esters in the final product, and such mixtures may be utilized without separation and isolation of the mono- or di-esters. If desired, the mono- or di-ester may be obtained in relatively pure form by subjecting the mixture of esters after reaction to fractional crystallization or selective extraction with a suitable solvent.

The esterification of the alcohol and citric acid may be conducted by any of the well known methods employed for the production of esters. However, it has been found desirable to produce these esters by a new method. In this method, a mono-hydric primary or secondary alkyl or alkylene alcohol conforming to the above noted formula may be reacted with citric acid monohydrate, by heating to an elevated temperature, such as 150° C. under reduced pressure until the reaction is complete. The reaction product for most purposes may be employed as such without further purification, or the mono- or di-ester, or both may be obtained from the reaction product by subjection to fractional crystallization or selective extraction with a suitable solvent. A solvent may be used, for example, which dissolves a monoester but does not dissolve any appreciable amount of the dia- and tri-esters, or alternately, a solvent may be employed which dissolves the di- and tri-ester but does not dissolve any appreciable quantities of the monoester. By repeating the treatment with the solvents, a relatively pure mono acid may be obtained. By the same means, the diester may be separated from the triester.

If it is desired to obtain a relatively pure monoester of citric acid, a monohydric primary alkyl or alkylene alcohol conforming to the formula noted above, may be reacted with anhydrous citric acid dissolved in a solvent, such as a dry pyridine containing concentrated sulfuric acid. About 0.75% of concentrated sulfuric acid based on the weight of the reaction mixture is used as the catalyst. For this purpose, the amounts of citric acid and alcohol employed are substantially those which favor the formation of the monoester. For this purpose, an amount of citric acid in excess of that required to react with the alcohol to produce the monoester is employed.

The reaction mixture is heated for a period of about four to six hours at about 100° C. after which the reaction mixture is maintained for a period of from fourteen to twenty hours at about 40 to 50° C. The resulting reaction product is then poured into a water-ice mixture containing a sufficient quantity of concentrated sulfuric acid to react with the pyridine in the mixture to form pyridine sulfate. A solvent such as low boiling petroleum ether in which the di- and triesters are relatively soluble but in which the monoester is relatively insoluble is employed to effect a separation of the monoester from the small amounts of the di- and tri-esters in the reaction mixture. The aqueous mixture is extracted first with ethyl ether in which the monoester as well as the di- and tri-esters is relatively soluble. To this ethyl ether extract is added a relatively large quantity of low boiling petroleum ether in which the monoester is substantially insoluble, but in which the di- and tri-esters are relatively soluble. This precipitates the monoester. If further purification is desired, this precipitate or oily residue is again dissolved in ethyl ether and the procedure repeated. Relatively pure diesters of citric acid may be prepared in a similar manner by reacting citric acid and the required alcohol in amounts which favor the formation of the diester. The diester may be separated from any monoester, such as a dry diester contained therein by fractional crystallization with a suitable solvent, such as ethanol.

Examples of mono- and di-esters of this invention are the citric acid esters of the following alcohols: 2 ethyl hexanol, octanols, decanols, dodecanols, hexadecanols, octadecanols, cosanols, docosanols, 2-ethyl hexenols, octenols, decenols, dodecenols, hexadecenols, octadecenols, cosenols and docosenols.

A more comprehensive understanding of this invention is obtained by reference to the following examples:

Example 1.—Mixture of monostearyl citrate, distearyl citrate and tristearyl citrate

A mixture of monostearyl citrate, distearyl citrate and tristearyl citrate which may be utilized for incorporating in margarine is prepared as follows: 12.1 kilos of citric acid monohydrate is added to 30 kilos of commercial stearyl alcohol (containing some palmityl alcohol) which is previously dissolved in the addition, the mixture is agitated. The mixture is held at 150° C. under reduced pressure for a period of 1½ hours. At the end of this period, boiling and foaming cease substantially. The resulting product which consists of a mixture of about 10 to 15% monostearyl citrate, about 50% distearyl citrate and the remainder tristearyl citrate together with a quantity of mono-, di- and tri-
palmityl citrates has an acid value of about 83, a saponification value of about 249 and a melting point of about 51 to 68°C. and a color on the Lovibond scale of about 35Y-5.8R.

Example 2.—Mixture of monolauryl citrate, di-
lauryl citrate and trilauryl citrate

A mixture of monolauryl citrate, dielauryl citrate and trilauryl citrate which may be also utilized for incorporation in margarine is prepared as follows:

A mixture of monolauryl citrate, dielauryl citrate and trilauryl citrate is prepared in a similar manner to that described in Example 1 for the preparation of the mixed monostearyl citrate. Except that 250 lbs. of commercial lauryl alcohol is used instead of the 30 kilos of commercial stearyl alcohol, and 120 lbs. of anhydrous citric acid is used instead of 12.1 kilos of citric acid monohydrate. The acid value of the mixture of about 15 to 20% monolauryl citrate, about 50% di-
lauryl citrate and the remainder trilauryl citrate is 118 and the saponification value is 314 compared respectively with theoretical values for pure dielauryl citrate of 106 and 318 respectively.

Example 3.—Pure monostearyl citrate

Pure monostearyl citrate is prepared as follows:

120 grams of anhydrous citric acid is dissolved in 200 grams of refined, dry pyridine containing 1.8 grams of concentrated sulfuric acid by mechanical agitation while heating on a steam plate at about 95°C. 20 grams of pure stearyl alcohol is then introduced. The stearyl alcohol is quite insoluble in the reaction mixture, a condition favoring monoster formation since a small concentration of stearyl alcohol in solution is reacted with a large excess of citric acid. The reaction mixture becomes homogeneous after about 4 hours, after which the reaction mixture is maintained at 49° to 50°C. for 16 hours.

The reaction mixture is poured into ice-cold water containing 78 grams of concentrated sulfuric acid. The aqueous mixture is extracted with ethyl ether and the ether extract is thoroughly washed with dilute hydrochloric acid and then with water and finally dried with anhydrous sodium sulfate. The ethyl ether solution of monostearyl citrate is evaporated, and the residue is crystallized several times from a petroleum ether, the boiling range of which is 89° to 112°C.

A typical melting point of the product is from 74 to 88.5°C., probably depending upon the proportion of symmetrical and unsymmetrical monostearils present. Other typical characteristics are:

<table>
<thead>
<tr>
<th>Acid Value</th>
<th>Found</th>
<th>Calcd.</th>
</tr>
</thead>
<tbody>
<tr>
<td>245</td>
<td>220</td>
<td>235</td>
</tr>
</tbody>
</table>

Example 4.—Mixture of monoisopropyl citrate and diisopropyl citrate

A mixture of about 50% monoisopropyl citrate and about 10% diisopropyl citrate is prepared as follows:

Equal parts of USP citric acid and anhydrous isopropyl alcohol are heated together under reflux, without catalyst for 118 hours at 92°C, after which time the acid value of the reaction mixture is found to be about 203.6 and the saponification value 392 (one-half esterified). The alcohol and most of the water of reaction are removed by low temperature evaporation in vacuo.

The residue is taken up with ethyl ether and then thrown out of the ether solution by the addition of a quantity of low-boiling petroleum ether just sufficient to form a precipitate. The precipitate or oily residue is again taken up with ethyl ether and the precipitation with low-boiling petroleum ether repeated. This procedure is repeated several times. After final removal of solvent by heating with stirring to 130°C, a typical analysis is:

<table>
<thead>
<tr>
<th>Acid Value</th>
<th>Found</th>
<th>Calcd.</th>
</tr>
</thead>
<tbody>
<tr>
<td>484</td>
<td>460</td>
<td>470</td>
</tr>
</tbody>
</table>

Example 5.—Mixture comprising principally dioleyl citrate, distearyl citrate and oleystearoyl citrate

A mixture of dioleyl citrate, distearyl citrate and oleystearoyl citrate is prepared as follows:

A mixture of 14 kilos of commercial oleyl alcohol and 14 kilos of commercial stearoyl alcohol is melted. To this mixture is added 10.2 kilos of anhydrous citric acid. During the addition, the mixture is agitated. The mixture is heated and held for a period of 11/2 hours at 150°C. under reduced pressure. At the end of this period, boiling and foaming cease substantially. The mixture contains the distearyl citrate, dioleyl citrate and their corresponding mono- and tri-esters together with mixed esters containing both stearoyl and oleyl groups such as oleystearoyl citrate.

Example 6.—Mixture of monooctyl citrate, dioctyl citrate and trioctyl citrate

A mixture of monooctyl citrate, dioctyl citrate and trioctyl citrate is prepared as follows:

150 lbs. of octyl alcohol (commercial 2-ethyl hexanol) is heated in a closed vessel with 137 lbs. of anhydrous citric acid for 6 1/2 hours at 150-155°C. The reaction product comprised three layers, an upper ester layer, a middle aqueous layer and an almost crystalline sponge. The upper oil layer which comprised mono-, di- and tri-octyl citrates was separated and deodorized for about 1 1/2 hours under reduced pressure at 150°C. The odorless and light-colored and limpid product was found to have an acid value of 147.6 and a saponification value of 435 compared with theoretical values for dioctyl citrate of 135 and 405 respectively. The mixture contained about 20% monooctyl citrate, about 40% dioctyl citrate and the remainder trioctyl citrate.

Example 7.—Pure distearyl citrate.

Substantially pure distearyl citrate is prepared by initially producing a mixture of monostearyl citrate, distearyl citrate and tristearoyl citrate as described in Example 1, and the distearoyl citrate is separated from the resultant reaction mixture by fractional crystallization from a suitable solvent such as ethanol or isopropanol, the tristearoyl citrate coming out of solution before the distearoyl citrate. The monostearoyl citrate is retained in solution.

The pure distearoyl citrate had an acid value of 76.4 and a saponification value of 240.2 (calculated acid value 80.6 and saponification value 242). Distearoyl citrate, upon supercooling, ex-
hibits a double melting point; one at 53° C. and a second melting point at 70 to 73° C.

The terms and expressions which we have employed are used as terms of description and not of limitation, and we have no intention, in the use of such terms and expressions, of excluding any equivalents of the features described or portions thereof, but recognize that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. An ester of citric acid selected from the class consisting of monoisopropyl citrate and monostearyl citrate.

2. Monoisopropyl citrate.

3. Monostearyl citrate.

References Cited

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

| UNITED STATES PATENTS | | |
|-----------------------|-------------------|
| Number                | Name              | Date |
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