

material with *p*-nitrophenyl sulfide, prepared from sodium sulfide and *p*-nitrochlorobenzene,<sup>13</sup> showed no depression. The yield was 23.6 g. (87%). After the substance had been recrystallized several times from glacial acetic acid, it melted at 160–161° (lit. 154°<sup>13</sup>).

*Anal.* Calcd. for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>S: C, 52.16; H, 2.90; N, 10.14. Found: C, 52.19; H, 2.82; N, 10.23.

### Summary

The low-melting material (m. p. ca. 135°) obtained from the crude product of the reaction of *p*-nitrochlorobenzene with sodium disulfide has been shown to be the eutectic mixture of two

moles of *p*-nitrophenyl sulfide and one mole of the disulfide. There thus appears to be no basis for the suggestion of Vorozhtzov and Kozlov that this material is an "angular" disulfide.

*p*-Nitrophenyl sulfide can be obtained in good yield by refluxing an alcoholic solution containing equivalent amounts of *p*-nitrochlorobenzene and potassium ethyl xanthate.

A convenient procedure for the preparation of *p*-nitrothiophenol has been described.

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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY<sup>1</sup>]

## The Higher Fatty Alcohol Esters of Gallic Acid

BY STEWART G. MORRIS AND R. W. RIEMENSCHNEIDER

Direct esterification of gallic acid with the lower alcohols up to six carbon atoms has been accomplished by various workers.<sup>2,3,4</sup> In most cases the gallic acid was esterified by an excess of the alcohol in the presence of either concentrated sulfuric acid or anhydrous hydrogen chloride as a catalyst. Attempts in this laboratory to apply these procedures in the preparation of the higher alcohol gallates resulted in very low yields of impure products. It has been reported<sup>5</sup> that the higher esters of gallic acid cannot be prepared by ordinary means. A search of the literature failed to reveal any description of the higher fatty alcohol esters of gallic acid.<sup>5a</sup>

Esterification of gallic acid with the polyalcohols has been effected by using galloyl chloride in which the hydroxyl groups have been protected as the tricarbomethoxy<sup>6</sup> and triacetyl<sup>7</sup> derivatives. Benzylolation as proposed by Schöpf and Winterhalder<sup>8</sup> offers an advantage over carbomethoxylation or acetylation, in that the benzyl groups can be more readily removed by hydrogenation.

In a preliminary study benzyl chloride, ethyl chloroformate and benzyl chloroformate were tried as a means of protecting the hydroxyl groups. The benzylated product was preferable because it could be more readily purified by crystallization. Clinton and Geissman<sup>9</sup> have shown

that on benzylolation better yields were obtained with methyl gallate than with gallic acid.

In the present work the hexyl, octyl, dodecyl, tetradecyl, hexadecyl and octadecyl gallates were prepared as follows: Gallic acid was esterified with methyl alcohol<sup>8</sup> and then benzylated.<sup>9</sup> The methyl tribenzyl gallate obtained was saponified to yield the free gallic acid tribenzyl ether. This was treated with thionyl chloride to form galloyl chloride tribenzyl ether, which was then esterified with the appropriate alcohol. The resulting ester was debenzylated.

### Experimental

**Galloyl Chloride Tribenzyl Ether.**—Into a 1-liter, round-bottom flask were introduced 44.0 g. (0.1 mole) of gallic acid tribenzyl ether<sup>9</sup> and 122 g. (1.2 moles) of thionyl chloride (distilled over beeswax), and the mixture was heated on a water-bath at 60° for one hour.<sup>8</sup> Then the excess of thionyl chloride, at a bath temperature of 60°, was removed at the water pump and the residue taken to dryness. (The recovered thionyl chloride can be reused.) To remove the last of the thionyl chloride from the reaction product, the residue was dissolved in benzene and again evaporated to dryness under diminished pressure. The product crystallized from benzene-petroleum ether mixture to yield 41.1 g. (90%) of galloyl chloride tribenzyl ether in white cottony needles, m. p. 116–116.5°.<sup>10</sup> On recrystallizing from benzene-petroleum ether, the crystals melted at 116.5–117°.

**Purification of Alcohols.**—Alcohols, none of which had a distillation range greater than 1.5°, were further purified by distilling them through a 75-cm. column packed with glass helices. The hexyl and octyl alcohols were distilled at atmospheric pressure; the others at about 1 mm. pressure. Only the constant boiling, middle cut of each alcohol was reserved for esterification work.

**Tribenzyl Gallate Esters.**—A typical experiment will be described. Ten grams of galloyl chloride tribenzyl ether (0.022 mole) and 9.4 g. (0.044 mole) of *n*-tetradecyl alcohol were placed in a 250-cc. Erlenmeyer flask and heated in an oil bath at 120°. The flask was shaken occasionally and removed from the bath as soon as the reagents had melted (ca. fifteen min.). After the bath had cooled to 90°, the

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) McKenzie and Müller, *J. Chem. Soc.*, **95**, 544 (1909).

(3) Christiansen, *THIS JOURNAL*, **48**, 1358 (1926).

(4) Russell and Tebbens, Jr., *ibid.*, **64**, 2274 (1942).

(5) Bergel, *Chemistry and Industry*, 127 (1944).

(5a) Since this paper was completed it has come to our attention that work is in progress on the evaluation of methyl, ethyl, propyl, amyl, hexyl, octyl, decyl and cetyl gallates as antioxidants for marine oils [see Editor's note, *Fishery Market News*, **7**, 7, 18 (1945)]. No method of preparation of these esters was given.

(6) Fischer, *Ber.*, **41**, 2882 (1908).

(7) Fischer, Bergmann and Lipschitz, *ibid.*, **51**, 45 (1918).

(8) Schöpf and Winterhalder, *Ann.*, **544**, 62 (1940).

(9) Clinton and Geissman, *THIS JOURNAL*, **65**, 85 (1943).

(10) The 76-mm. immersion thermometer used for all melting point determinations was calibrated against a 76-mm. immersion thermometer which had been certified by the U. S. Bureau of Standards.

TABLE I  
 ALKYL ESTERS OF 3,4,5-TRIS-(BENZYLOXY)-BENZOIC ACID

Alkyl	Yield, %	M. p., °C.
<i>n</i> -Hexyl	80	72-73
<i>n</i> -Octyl	84	74.5
<i>n</i> -Dodecyl	86	71.5-72
<i>n</i> -Tetradecyl	89	75.5-76
<i>n</i> -Hexadecyl	85	79.5-80
<i>n</i> -Octadecyl	84	83.5-84

Absolute alcohol was added to make a total volume of about 150 cc. This solution was heated in a steam-bath nearly to boiling temperature to dissolve the sample. By starting the hydrogenation immediately on removing the bottle from the bath, the sample could be hydrogenated before the alcohol cooled sufficiently to permit crystallization of the sample. On the other hand, the reduced sample was readily soluble in the alcohol at room temperature. The hydrogenation was usually completed within five to ten minutes. The alcohol solution was then rewarmed and filtered from the palladium-charcoal catalyst.

 TABLE II  
 ESTERS OF GALLIC ACID

Alkyl	Yield, %	M. p., °C.	Empirical formula	Analyses, %			
				Calcd.		Found	
				C	H	C	H
<i>n</i> -Hexyl	84	93.5	C <sub>13</sub> H <sub>18</sub> O <sub>5</sub>	61.40	7.13	61.68	7.47
<i>n</i> -Octyl	95	94-95	C <sub>15</sub> H <sub>22</sub> O <sub>5</sub>	63.80	7.85	63.85	7.76
<i>n</i> -Dodecyl	88	96.5-97	C <sub>19</sub> H <sub>30</sub> O <sub>5</sub>	67.40	8.94	67.46	8.80
<i>n</i> -Tetradecyl	90	98.5-99.2	C <sub>21</sub> H <sub>34</sub> O <sub>5</sub>	68.80	9.35	68.76	9.10
<i>n</i> -Hexadecyl	86	99.5-100	C <sub>23</sub> H <sub>38</sub> O <sub>5</sub>	70.00	9.71	70.17	9.73
<i>n</i> -Octadecyl	79	104.5	C <sub>25</sub> H <sub>42</sub> O <sub>5</sub>	71.05	10.02	71.11	10.00

flask was returned, and this temperature was maintained for an additional hour. Then the flask was removed, 200 cc. of petroleum ether (30-70° b. r.) was added, and the mixture was stirred vigorously. By adding the petroleum ether to the warm molten product it was possible to effect complete solution before crystallization began. After crystallization was complete, the ester was filtered and washed with petroleum ether. The product was redissolved in a minimum of warm petroleum ether and filtered through a sintered glass funnel under pressure. The clear filtrate yielded a well-defined crystalline product.

The melting points and the per cent. yields of the various tribenzyl gallates (3,4,5-tris-benzyloxy-benzoic acid esters) prepared by the procedure described above are shown in Table I. The yields represent the amount of product recovered after two crystallizations.

Two points regarding the esterification should be emphasized. There should be an excess of the alcohol. If molecular equivalents of the alcohol and the galloyl chloride tribenzyl ether are used, some of the latter will contaminate the ester and make purification difficult. The reaction should not be carried out at too high a temperature. When the entire esterification was conducted at 120°, for example, the yields of ester were lowered, and purification was complicated.

**Debenzylations.**—The tribenzyl gallate derivatives were debenzylated by catalytic hydrogenation at 35-45 lb. pressure gage reading. Eight to twelve grams of the sample, depending upon its solubility in warm alcohol, the lower esters being more soluble, and 4 to 6 g. of palladium-charcoal<sup>11,12</sup> were placed in the hydrogenation bottle.

The catalyst can be reused a number of times; 6 g. remained active after being used in thirty hydrogenation operations. Between reductions of samples differing chemically, the catalyst was heated with absolute alcohol and filtered in order to remove any compounds adhering to the charcoal from the previous reduction. The catalyst was stored in a desiccator.

**Gallate Esters.**—The alcohol filtrate containing the reduced sample was taken to dryness on a water bath under diminished pressure. The residue was re-dissolved in absolute ether and again taken to dryness in order to remove all the alcohol. Any alcohol remaining with the product would impede crystallization later. The gallate was purified by two crystallizations from petroleum ether-benzene solvent. The properties of the gallates prepared are listed in Table II.

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### Summary

The normal hexyl, octyl, dodecyl, tetradecyl, hexadecyl and octadecyl esters of gallic acid have been prepared and characterized. They were obtained by first preparing the corresponding esters of 4,5,6-tris-(benzyloxy)-benzoic acid and then debenzylating them by catalytic hydrogenation.

(11) Baltzly and Buck, *THIS JOURNAL*, **65**, 1984 (1943).

(12) Ott and Schröter, *Ber.*, **60**, 633 (1927).