TABLE I

DATA FOR THE CATION EXCHANGE REACTION, $Ba^{++} + UO_2R_2 \rightleftarrows BaR_2 + UO_2^{++}$ AT 25°

Molality, m	Exchange[a] constant $K_{ex.}$	Activity[b] coefficient of uranyl nitrate (binary solution) $\gamma_\pm$	Activity[c] coefficient of barium nitrate (binary solution) $\gamma_\pm$	Calcd. activity coefficient of barium nitrate (ternary solution) $\gamma_\pm$
0	(14)	1.0	1.0	1.00
0.01	10.8	0.80	0.71	0.73
.02	10.0	.75	.63	.67
.04	8.95	.69	.55	.59
.06	8.40	.66	.50	.56
.08	8.15	.64	.46	.53
.10	8.00	.60	.43	.50
.20	7.70	.57	.34	.47
.30	7.55	.57	.29	.46
.40	7.30	.57	.26	.46
.50	7.05	.55	(.24)	(.44)

[a] The exchange constant $K_{ex.}$ is for solutions containing $UO_2(NO_3)_2$ at the stated molalities and $Ba(NO_3)_2$ in tracer quantities (*ca.* 10^{-8} molal). Values for $K_{ex.}$ were read from a smooth curve drawn through the experimental data. The observed average deviation was ±5%. The value of $K_{ex.}$ for $m = 0$ was obtained by extrapolation. [b] Landolt-Börnstein, "Tabellen," Erg. II, Part 2, Fifth Ed., p. 1129 (1931); R. A. Robinson, THIS JOURNAL, **64**, 1469 (1942). [c] Landolt-Börnstein, "Tabellen," Erg. III, Part 3, Fifth Ed., p. 2141 (1936); R. H. Stokes, *Trans. Faraday Soc.*, **54**, 295 (1948).

change resins (*e.g.*, Dowex 50 or Amberlite IR-120), so that the capacity of the ion exchange resin is independent of *p*H. Since both exchanging cations were of the same valence in the present study, it is reasonable to expect that changes in resin capacity because of varying *p*H are largely cancelled. The activity of the ions in the resin phase is a point of uncertainty. It appears safe to assume, however, that for the conditions employed in this investigation the activity of the cations in the resin phase is equal to their mole fractions.

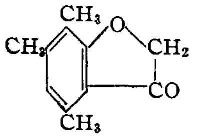
Acknowledgments.—The author is indebted to J. W. Richter, now associated with Merck and Co., Rahway, New Jersey, for technical assistance, and to T. F. Young of the University of Chicago for helpful discussions.

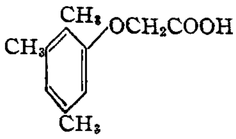
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENN.
RECEIVED MARCH 21, 1951

2,4,5-Trimethyl-6-hydroxybenzoic Acid

BY LEE IRVIN SMITH AND RICHARD REMSEN HOLMES

Some time ago there was described preparation of 4,6,7-trimethylcoumaran-3-one (I) by action of sulfuric acid upon 2,3,5-trimethylphenoxyacetic acid (II).[1] The structure of I was established beyond any doubt, but ozonolysis of III, the isopropylidene derivative of I, led to a trimethylsalicylic acid melting at 181–182°. In conformity with the structure assigned to I, this acid was regarded as 2,4,5-trimethyl-6-hydroxybenzoic acid (IV). But an acid, supposed to be IV, had been prepared by Jacobsen and Schnapauff[2] by fusion of durenol with alkali, and this acid was reported to melt at 148°. The


I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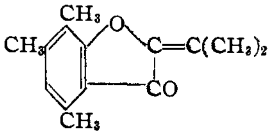
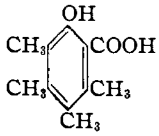
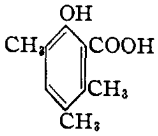
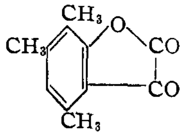

III


IV


V


VI

isomeric acid, 2,3,5-trimethyl-6-hydroxybenzoic acid (V) had been prepared by Krohn *via* Kolbe synthesis from 2,4,5-trimethylphenol, and reported to melt at 181°.[3] Hence, it appeared that the salicylic acid obtained by ozonolysis of III was V and not IV, and the possibility of migration of a methyl group during cyclization of II to I had to be considered. Krohn's work was repeated and his acid melting at 181° was obtained. But a mixed melting point of Krohn's acid with the acid IV obtained from III showed that the two were not identical, and made it clear that IV was actually 2,4,5-trimethyl-6-hydroxybenzoic acid. It, therefore, became necessary to assume either that Jacobsen and Schnapauff had not actually prepared IV, or else this acid existed in polymorphic forms.

Since the earlier work[1] durenol has become available, and in order to clear up the uncertainty regarding the structure of IV, the work of Jacobsen and Schnapauff was repeated. Fusion of durenol with alkali, as described by these authors, led to a trimethylsalicylic acid melting at 184°, together with a small amount of a hydroxydibasic acid melting at 276–280° (dec.). It thus appears that there is a typographical error in the paper of Jacobsen and Schnappauf, and that the melting point given there for IV—and of course copied by Beilstein—as 148° should have read 184°. Additional evidence that the structure of I is correct has been provided[4] by conversion of I to the same coumarandione VI as that obtained by action of oxalyl chloride upon 2,3,5-trimethylphenol.

Experimental Part

A mixture of durenol (19 g., m.p. 117°) and potassium hydroxide (150 g.) was fused in a large nickel crucible. The melt was stirred and kept at 180–220° for two hours; evolution of gas (hydrogen) was steady, and at the end of the reaction the dark upper layer of potassium phenolate disappeared. The melt was dissolved in water (1.5 l.) and the solution was acidified. Separation of a very small amount of durenol (m.p. 117°) occurred; this was removed and the filtrate was extracted with three 100-cc. portions of benzene. The combined benzene solutions were extracted several times with aqueous sodium bicarbonate (5%). Acidification of the bicarbonate extracts produced a white solid which, after crystallization from aqueous ethanol, melted at 184°.

Anal. Calcd. for $C_{10}H_{12}O_3$: neut. equiv. (one), 180. Found: neut. equiv., 188.

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[1] L. I. Smith, J. A. King, C. O. Guss and J. Nichols, THIS JOURNAL, **65**, 1594 (1943).

[2] O. Jacobsen and E. Schnapauff, *Ber.*, **18**, 2841 (1885).

[3] C. Krohn, *ibid.*, **21**, 884 (1888).

[4] L. I. Smith and R. R. Holmes, THIS JOURNAL, **73**, 4294 (1951).

The aqueous layer coming from the previously described benzene extraction was extracted with three 150-cc. portions of ether and the combined extracts were dried (sodium sulfate). Evaporation of the ether left a residue (0.2 g.) which was very soluble in water. It was crystallized from a mixture of ethyl acetate and petroleum ether (b.p., 60–68°), when it formed white plates melting at 276–280° (dec.). The value for the neutral equivalent indicated that this substance was a dimethyldicarboxyphenol.

Anal. Calcd. for $C_{10}H_{10}O_6$: neut. equiv. (two), 105. Found: neut. equiv., 107.

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Esters of Glucose and Lactose

BY J. H. SCHWARTZ AND E. A. TALLEY

A number of straight-chain aliphatic acid esters of glucose and lactose were prepared. The crystalline compounds are described below; the others are listed in Table I.

TABLE I

PROPERTIES OF POLYSUBSTITUTED GLUCOSE AND LACTOSE ESTERS

Ester	Acyl groups per mol.[a]	Elementary analyses, % Calcd.[b] C	H	Found[c] C	H	Free acidity,[d] %	$[\alpha]^{26}D$ (c, 2.5) in $CHCl_3$	M.p., °C. (cor.)	$n^{20}D$	Physical state and color
A. Glucose										
Caprylate	4.7	67.7	10.2	68.2	10.2	1.1	+46.8		1.4587	Light-amber sirup
Caprate	4.8	70.5	10.8	70.9	10.8	1.1	+40.3		1.4612	Light-amber sirup
B. Lactose										
Caproate	7.2	63.2	9.0	63.2	9.0	0.85	+15.3		1.4646	Light-yellow sirup
Caprylate	6.9	66.5	9.9	66.7	10.2	1.5	+14.5		1.4650	Amber sirup
Caprate	7.0	69.3	10.5	69.6	10.7	2.0	+12.6		1.4657	Amber sirup
Laurate	6.5	70.7	10.9	70.2	11.1	Trace	+13.4	110–112		White, waxy solid
Myristate	7.2	73.0	11.4	73.3	11.4	0	+ 9.4	43.4–46.0		White, waxy solid
Palmitate	7.5	74.5	11.7	74.5	11.7	Trace	+ 9.0	55.6–58.2		White, waxy solid
Stearate	7.2	75.4	11.9	75.3	12.0	Trace	+ 7.9	62.5–64.5		White, waxy solid

[a] Calculated from free hydroxyl values obtained by the method of Ogg, Porter and Willits, *Ind. Eng. Chem., Anal. Ed.*, 17, 394 (1945). [b] Based on the number of acyl groups per mol. found. [c] Microanalyses by C. L. Ogg and Mary Jane Welsh. [d] By Mrs. R. B. Kelly.

All the esters but the lactose butyrate were prepared by slowly adding a chloroform solution of acid chloride (10% excess) to a stirred mixture of the sugar (β-lactose, or anhydrous α-glucose), pyridine (1.1 moles/mole of acid chloride), and chloroform.[1] After initially cooling with an ice-salt mixture (until one hour after the acid chloride was added) the reaction was carried out six to eight hours at room temperature for the glucose esters and four to thirteen hours at 50–70° for the lactose, depending upon the reaction rate.

α-D-**Glucose Pentamyristate.**—After three recrystallizations from an alcohol–chloroform mixture the ester formed long, fine needles, insoluble in 95% alcohol and acetone, soluble in Skellysolve C and very soluble in ether, chloroform and benzene; m.p. 59.0–59.8° (cor.), $[\alpha]^{25}D$ +38.3° (*c* 2.5, chloroform), +33.5° (*c* 2.5, benzene).

Anal. Calcd. for $C_6H_7O_6(COC_{13}H_{27})_5$: free hydroxyl, none; C, 74.09; H, 11.62. Found: free hydroxyl, none[2a]; free acidity, none[2a]; C, 74.19; H, 11.63.[2b]

Lactose Octabutyrate[3] (β?).—β-Lactose was stirred with a mixture of butyric anhydride (70% excess) and pyridine (1.9 moles/mole of butyric anhydride) for eight hours at room temperature, eight hours at 50°, and 23 hours at 90°. After separating the crystals which formed in the sirupy product and recrystallizing four times from a 3:1 alcohol-water mixture, the ester was obtained as fine needles very soluble in 95% alcohol, acetone, Skellysolve C, ether, chloroform and benzene; m.p. 77.0–77.4° (cor.), $[\alpha]^{25}D$ + 4.6° (*c* 2.5, chloroform), −14.2° (*c* 2.5, benzene).

Anal. Calcd. for $C_{12}H_{14}O_{11}(COC_3H_7)_8$: free hydroxyl, none; C, 58.52; H, 7.81. Found: free hydroxyl, none[2a]; free acidity, none[2a]; C, 58.55; H, 8.17.[2b]

EASTERN REGIONAL RESEARCH LABORATORY[4]
PHILADELPHIA, PENNA.
RECEIVED JANUARY 27, 1951

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[1] *Cf.* G. Zemplén and E. D. Laszlo, *Ber.*, **48**, 915 (1915).

[2] (a) By Mrs. R. B. Kelly. (b) Microanalyses by C. L. Ogg and Mary Jane Welsh.

[3] An apparently unsuccessful preparation was recorded by M. Berthelot, *Ann. chim. phys* [3] **60**, 98 (1860).

[4] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

X-Ray Investigation of *t*-Butyl Chloride and *t*-Butyl Bromide[1]

BY ROBERT S. SCHWARTZ, BENJAMIN POST AND I. FANKUCHEN

Thermal measurements indicate that both *t*-butyl chloride and *t*-butyl bromide undergo two transitions in the solid state. The sum of the entropies of the transitions is 8.7 e.u./mole for the chloride, and 7.6 e.u./mole for the bromide. The dielectric constants of the crystalline solids just below the melting point are higher than those of the liquids.[2,3] These data indicate that both crystalline solids are highly disordered above the transition temperatures. The nature of the disorder has been investigated using low temperature single crystal X-ray diffraction techniques.

Experimental

Eastman Kodak Co. "white label" *t*-butyl chloride and *t*-butyl bromide were fractionally distilled in a column packed with glass helices. The fraction of *t*-butyl chloride boiling between 50.0–50.5° was used; $n^{20}D$ 1.3852. The *t*-butyl bromide boiled at 72.7–73.0°; $n^{20}D$ 1.4278.

Optical observations indicate that both compounds are isotropic at temperatures above transition II and strongly birefringent below this transition. Baker and Smyth,[2] however, have reported that below this transition crystalline *t*-butyl bromide is isotropic.

Samples of the compounds were sealed in thin-walled Pyrex capillary tubes and mounted on the goniometer arcs of a low temperature X-ray camera.[4] Single crystals of the

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[1] This work supported by the Office of Naval Research.

[2] W. O. Baker and C. P. Smyth, THIS JOURNAL, **61**, 2798 (1939).

[3] L. M. Kushner, R. W. Crowe and C. P. Smyth, *ibid.*, **72**, 1091 (1950).

[4] B. Post, R. S. Schwartz and I. Fankuchen, *Rev. Sci. Inst.*, **22**, 218 (1951).