TABLE I

THALLOUS SULFONATES

Thallous salt	M. p., °C.	Formula	Tl analyses, %[4] Calcd.	Found
Sulfamate	139–140	H_2O_3NSTl	68.0	68.0
o-Toluenesulfonate	213–216	$C_7H_7O_3STl$	54.3	54.3
p-Toluenesulfonate	226–228	$C_7H_7O_3STl$	54.3	54.1
p-Bromobenzenesulfonate	274–276	$C_6H_4O_3BrSTl$	46.3	46.3
m-Nitrobenzenesulfonate	307–309	$C_6H_4O_5NSTl$	50.3	50.2
Sulfanilate	207–209	$C_6H_6O_3NSTl$	54.3	54.2
2-Bromotoluene-4-sulfonate	220–222	$C_7H_6O_3BrSTl$	44.8	44.5
2-Aminotoluene-4-sulfonate	101–103	$C_7H_8O_3NSTl$	52.3	52.1
2-Naphthoquinone-4-sulfonate	228–232 dec.	$C_{10}H_6O_4STl$	47.9	47.6
d-Camphorsulfonate	267–269	$C_{10}H_{15}O_4STl$	46.8	46.6
1,2,3,4-Tetramethylbenzene-5-sulfonate[5]	260–262	$C_{10}H_{13}O_3STl$	49.0	48.7
1,2,3,5-Tetramethylbenzene-4-sulfonate[5]	283–285	$C_{10}H_{13}O_3STl$	49.0	48.9
1,2,4,5-Tetramethylbenzene-3-sulfonate[6]	340–341 dec.	$C_{10}H_{13}O_3STl$	49.0	48.8
Pentamethylbenzenesulfonate[5]	325–326	$C_{11}H_{15}O_3STl$	47.3	47.1

The sulfonic acid is readily regenerated from the thallous salt by acidification with hydrochloric acid.

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(4) Meyer and Bertheim, *Ber.*, **37**, 2051 (1904).

(5) The authors wish to thank Dr. L. I. Smith for samples of these sodium sulfonates. The melting points reported in Table I are uncorrected.

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The Catalytic Reduction of Dehydrocholic Acid in Presence of Raney Nickel

BY W. M. HOEHN AND H. E. UNGNADE

Dehydrocholic acid has been reduced with palladium and hydrogen in acetic acid, with aluminum amalgam with benzene and ether as the solvent,[1] with sodium amalgam[2] and electrolytically.[3] Ethyl dehydrocholate has been reduced with hydrogen in the presence of a catalyst consisting of nickel or cobalt.[4]

Biological systems also have been studied and it has been found that reductodehydrocholic acid,[5] isoreductodehydrocholic acid[6,7] and 7-hydroxy-3,12-diketocholanic acid,[8] were formed from dehydrocholic acid.

It has now been found that reductodehydrocholic acid is the main product when dehydrocholic acid is reduced in methanol solution with hydrogen in the presence of Raney nickel. Other compounds that have been isolated from the mixture were methyl dehydrocholate and methyl reductodehydrocholate. Yields of reductodehydrocholic acid as high as 85% of the theoretical amount may be obtained when the reduction of dehydrocholic acid in methanol solution is carried out at 105°, under a hydrogen pressure of 3800 lb. No further reduction of reductodehydrocholic acid was observed when it was submitted to a hydrogen pressure of 5800 lb. at a temperature of 230°.

Two typical runs are listed in the following table

Moles of dehydrocholic acid	T, °C.	P	Time, hr.	Products isolated
0.1	110	3800	3	67% reductodehydrocholic acid 20% methyl reductodehydrocholate 12% methyl dehydrocholate
0.2	105	3800	5	85% reductodehydrocholic acid 5% dehydrocholic acid 10% mixture of esters

Physical constants of the pure compounds

Reductodehydrocholic acid, m. p. 187–188° $[\alpha]^{25}\text{D} = +30 \pm 1$

Methyl dehydrocholate, m. p. 232–233° $[\alpha]^{25}\text{D} = +30 \pm 1$

Methyl reductodehydrocholate, m. p. 152–153° $[\alpha]^{25}\text{D} = +32 \pm 1$

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(1) Borsche and Hallwass, *Ber.*, **55**, 3318 (1922).

(2) Schenck, *Z. physiol. Chem.*, **69**, 383 (1910).

(3) Schenck, *ibid.*, **63**, 308 (1909).

(4) Bockmühl, Ehrhart and Ruschig, U. S. Patent 2,143,676 (1939).

(5) Kyoguku, *Z. physiol. Chem.*, **250**, 253 (1937).

(6) Shibuya, *J. Biochem.* (Japan), **17**, 385 (1933).

(7) Yamosaki and Kyoguku, *Z. physiol. Chem.*, **233**, 29 (1935); **235**, 443 (1935).

(8) Mori, *J. Biochem.* (Japan), **29**, 87 (1939).