semicarbazone, m.p. 176°.[9] (IVc) could not be obtained by the same procedure and the following procedure was conducted:

To a stirred suspension of 70 g. (0.376 mole) of (IIIc) in 200 cc. of benzene, 144 cc. (0.36 mole) of 15% AcOH (85% water) was added at room temperature, and the reaction mixture was heated to 70~80° for ca. 1 hr. until the evolution of CO_2 ceased. Water was added, the mixture was extracted with benzene, and the benzene layer was treated in the usual way to give ca. 35 g. of crude phenylacetaldehyde, which was used for the hydrogenation. The pure aldehyde: $b.p_7$ 73° (yield, 50%)[5]; oxime,[10] m.p. 98°.

3, 4-Dimethoxyphenethyl Alcohol (Va)—A solution of 47.5 g. of crude (IVa) in 200 cc. of EtOH was hydrogenated over 15 g. of Raney Ni (W-2) at an initial pressure of 40 atm. of hydrogen at 40° for 3 hrs. until more than the calculated amount of H_2 was taken up. The filtered solution was evaporated *in vacuo*, the remaining oil was dissolved in benzene, washed with satd. NaCl solution, dried over Na_2SO_4, and benzene was removed. The residual oil was distilled, giving a colorless oil of $b.p_4$ 145~150°. Yield, 38 g. (62.3% from (IIIa)). The purified alcohol solidified on standing at room temperature, m.p. 48°.[1]

In a similar way, 3, 4-methylenedioxyphenethyl alcohol (Vb)[2] of $b.p_4$ 135~136° was obtained in the yield of 54.7% from (IIIb), and phenethyl alcohol (Vc)[11] of $b.p_{12}$ 98~100° in the yield of 48% from (IIIc).

Summary

3, 4-Dimethoxyphenethyl alcohol and 3, 4-methylenedioxyphenethyl alcohol were respectively prepared from veraltraldehyde and piperonal in a four-step process involving Darzens reaction with the over-all yield of 45~50%.

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Shigeru Yoshida and Mitsuru Kataoka: Studies on the Allied Compounds of Vitamin B_1. XXIII.[1] Synthesis of N-Acyl-O,S-dibenzoylthiamines.

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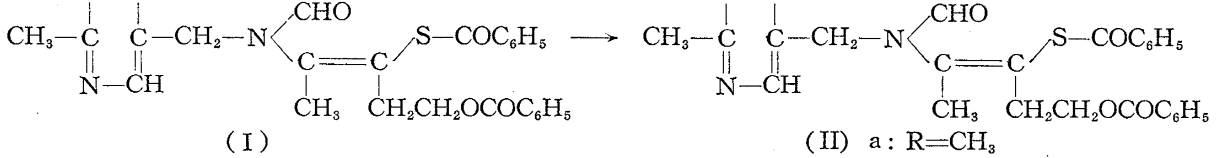
N-Acylation of thiothiamine and tetrahydrofurothiothiamine was described in the preceding paper[1] and for the same purpose of preparing N-acylated thiamine derivatives, the same reaction as before was carried out on O,S-dibenzoylthiamine[2] (I), from which N-acyl-O,S-dibenzoylthiamines (II) were obtained. Of the various acylated derivatives, only N-acetyl derivative (IIa: $R=CH_3$) was obtained in crystalline state, and N-propionyl (IIb: $R=C_2H_5$) and N-butyroyl (IIc: $R=C_3H_7$) were characterized as their crystalline picrates, respectively melting at 148° and 160°. Repeated recrystallization of the picrate resulted in deacylation, with increasingly higher melting point, and the final product was identified with O, S-dibenzoylthiamine picrate.



(I)

(II) a: $R=CH_3$
b: $R=C_2H_5$
c: $R=C_3H_7$

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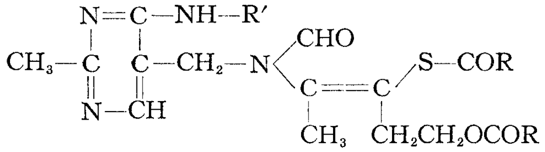
[1] Part XXII: This Bulletin, **6**, 527(1958).
[2] S. Yoshida: Yakugaku Zasshi, **74**, 993(1954); T. Matsukawa, H. Kawasaki: *Ibid.*, **73**, 705, 709(1953).

The structure of N-acetyl-O, S-dibenzoylthiamine (IIa: R=CH_3) is certain from its infrared absorption spectrum, as listed in Table I. It has an absorption of $\nu_{(NH)}$ at 3236 cm^{-1}, but no $\delta_{(NH_2)}$, and an absorption of amide-I at 1730 cm^{-1}. In order to clarify the absorption of O, S-diacylthiamine, that of propyl thiamine disulfide is also given in Table I.

TABLE I. Infrared Spectra of O,S-Diacylthiamine Derivatives (in Nujol)



Compound		$\nu_{(NH)}$ (cm^{-1})	CO-absorption (cm^{-1})				$\delta_{(NH_2)}$ (cm^{-1})
R	R′		Amide-I	Ester band	Thiol ester band	N-CHO band	
CH_3	H	3378, 3175		1745	1701	1672	1661
C_6H_5	H	3497, 3335		1712	1684	1672	1661
C_6H_5	$COCH_3$	3236	1730	1695	1681	1664	
Propyl thiamine disulfide	(a)	3335, 3125				1672	1655
	(b)	3509, 3344 3215 ($CHCl_3$) (0.1-mm. cell)				1656	1637

The authors are indebted to Messrs. Shindo and Amakasu for infrared spectral measurements and to Misses Furukawa and Ohtsuka for elemental analyses.

Experimental

N-Acetyl-O, S-dibenzoylthiamine (IIa: R=CH_3)—i) A mixture of 1.5 g. of (I), 3 g. of Ac_2O, and 5 cc. of benzene was warmed at 80~85° for 3 hrs., cooled, and benzene and excess of Ac_2O were distilled off at a reduced pressure. The residue was left to stand in a refrigerator of −5° to −10°, by which it turned crystalline. The crystals were collected by filtration and recrystallized four times from EtOH to 1 g. of crystals melting at 103°. *Anal.* Calcd. for $C_{28}H_{28}O_5N_4S$: C, 63.15; H, 5.25; N, 10.50. Found: C, 63.39; H, 5.27; N, 10.45.

Addition of EtOH solution of picric acid to EtOH solution of (IIa) afforded a yellow picrate melting at 141°. *Anal.* Calcd. for $C_{28}H_{28}O_5N_4S \cdot C_6H_3O_7N_3$: C, 52.29; H, 4.07; N, 12.87. Found: C, 52.40; H, 4.37; N, 12.38.

ii) A mixture of 1.5 g. of (I) and 10 cc. of AcCl was warmed on a water bath at 70~80° for 10 mins. and AcCl was distilled off under a reduced pressure. The residue was allowed to stand in a refrigerator overnight and crystalline solid so formed was recrystallized from EtOH to 0.7 g. of (IIa), m. p. 103°.

N-Propionyl-O, S-dibenzoylthiamine (IIb: R=C_2H_5)—A mixture of 1.5 g. of (I), 2 g. of propionic anhydride, and 5 cc. of benzene was treated as for (IIa), and the uncrystallizable product was derived to its picrate of m. p. 148°. *Anal.* Calcd. for $C_{29}H_{30}O_5N_4S \cdot C_6H_3O_7N_3$: C, 54.19; H, 4.25; N, 12.64. Found: C, 53.76; H, 4.15; N, 12.70.

N-Butyroyl-O, S-dibenzoylthiamine (IIc: R=C_3H_7)—Prepared in a similar manner as above and the product also failed to crystallize. It formed a picrate of m. p. 160°. *Anal.* Calcd. for $C_{30}H_{32}O_5N_4S \cdot C_6H_3O_7N_3$: C, 54.75; H, 4.43; N, 12.42. Found: C, 54.47; H, 4.33; N, 11.78.

Summary

N-Acyl-O,S-dibenzoylthiamines (II) were prepared by the application of acid anhydride to O,S-dibenzoylthiamine (I).

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