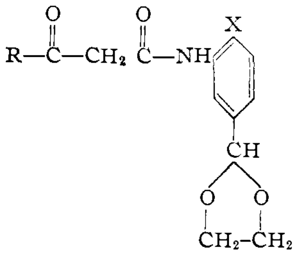
TABLE I

3-ACYLACETAMIDOBENZALDEHYDE ETHYLENE GLYCOL ACETALS



R	X	M.p., °C.	Empirical formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	Max. absorption,[a] mμ
C_6H_5	H	91–92	$C_{18}H_{17}O_4N$	69.45	69.37	5.47	5.59	4.50	4.64	443
C_6H_5 (aldehyde)	H	101–102.5	$C_{16}H_{13}O_3N$	71.91	...	4.87	..	5.24	...	
2-$CH_3OC_6H_4$	H	116–118	$C_{19}H_{19}O_5N$	66.82	66.91	5.61	5.81	4.11	4.37	422
4-$CH_3OC_6H_4$	H	.....	$C_{19}H_{19}O_5N \cdot H_2O$	63.47	63.49	6.03	5.95	3.90	3.91	443
2-$C_6H_5OC_6H_4$	H	101–103	$C_{24}H_{21}O_5N$	71.43	70.95	5.25	5.59	3.47	3.86	430
4-$C_6H_5OC_6H_4$	H	Oil	$C_{24}H_{21}O_5N$	71.43	...	5.25	..	3.47	...	
2-ClC_6H_4	H	Oil	$C_{18}H_{16}O_4NCl$	62.50	...	4.67	..	10.24	...	
2-ClC_6H_4 (aldehyde)	H	99–101	$C_{16}H_{12}O_3NCl$	63.66	63.57	4.01	4.14	11.75	11.98	440
4-ClC_6H_4	H	142–144	$C_{18}H_{16}O_4NCl$	62.50	62.33	4.67	4.75	10.24	10.39	441
2,4-$Cl_2C_6H_3$	H	Oil	$C_{18}H_{15}O_4NCl_2$	56.84	...	3.95	..	3.68	...	
2,4-$Cl_2C_6H_3$ (aldehyde)	H	146–147	$C_{16}H_{11}O_3NCl_2$	57.14	57.34	3.30	3.39	21.10	21.11	440
4-$C_2H_5OCOC_6H_4$	H	141.5–142	$C_{21}H_{21}O_6N$	65.80	65.86	5.48	5.57	3.66	3.64	440
4-$C_2H_5OCOC_6H_4$ (aldehyde)	H	152.5–153	$C_{19}H_{17}O_5N$	67.26	67.10	5.01	5.07	4.13	4.10	
4-$HOOCC_6H_4$	H	184–185	$C_{19}H_{17}O_6N$	64.23	...	4.79	..	3.94	...	
C_6H_5	CH_3	155.5–156	$C_{19}H_{19}O_4N$	70.15	70.48	5.85	6.16	4.31	4.32	440
C_6H_5 (aldehyde)	CH_3	151.5–152	$C_{17}H_{15}O_3N$	72.60	72.56	5.34	5.68	4.98	4.95	
C_6H_5	CH_3O	97–98	$C_{19}H_{19}O_5N$	66.86	66.75	5.57	5.69	4.11	4.16	442
CH_3	H	86–86.5	$C_{13}H_{15}O_4N$	62.65	62.79	6.02	6.47	5.62	5.35	441
CH_3 (aldehyde)	H	96.5–97.5	$C_{11}H_{11}O_3N$	64.39	64.25	5.37	5.33	6.83	6.84	
CH_3	CH_3	86–89	$C_{14}H_{17}O_4N$	63.88	...	6.46	..	5.32	...	
CH_3	CH_3O	101–101.5	$C_{14}H_{17}O_5N$	60.21	60.36	6.09	6.24	5.02	5.00	
C_2H_5O	H	Oil	$C_{14}H_{17}O_5N$	60.21	...	6.09	..	5.02	...	
C_2H_5O	CH_3	99–99.5	$C_{15}H_{19}O_5N$	61.43	61.21	6.48	6.73	4.78	4.80	440
C_2H_5O	CH_3O	79.5–80.5	$C_{16}H_{19}O_6N$	58.25	...	6.15	..	4.53	4.2	440
C_2H_5O (aldehyde)	CH_3O	119.5–120.5	$C_{13}H_{15}O_5N$	58.87	58.83	5.66	5.78	5.28	5.31	

[a] Of the yellow photographic dye from oxidized *p*-aminodiethylaniline.

Preparation of Polyvinyl Acetals.—A mixture of 0.034 mole of the 3-acylacetamidobenzaldehyde ethylene glycol acetal, 0.009 mole of sodium benzaldehyde-*o*-sulfonate monohydrate, 50 ml. of water, 250 ml. of ethanol, 3 ml. of 85% phosphoric acid and 50 g. (0.57 mole) of polyvinyl alcohol was stirred at 75–80° for one hour, cooled and diluted with 300 ml. of acetone. The polymer was collected on a filter. It was then suspended in methanol and neutralized with triethylamine, filtered and then resuspended in methanol and finally twice in acetone. After drying, the product usually weighed about 55 g. and contained 8 to 10% of color-forming acetal groups by weight and 3% of solubilizing acetal groups.

CONTRIBUTION NO. 348 FROM THE CHEMICAL DEPARTMENT
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Steam-Volatile Fatty Acids from a Marine Tube Worm

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RECEIVED MARCH 1, 1954

The unique five-carbon fatty acids, α-methylbutyric and tiglic, have been isolated along with acetic, propionic, butyric and *n*-valeric acids from parasitic hog worms.[1–3] The method of formation and metabolic pathways of these acids in worms is unknown. Intestinal worms are heavily contaminated with bacteria but it has been shown that after these worms have been rendered "bacteria free" the acids are still produced.[1,3,4]

The marine tube worm *Eudistylia vancouveri* grows abundantly on the shore of Brockton Point at Vancouver, British Columbia, and at a few other west coast locations. Recently *n*-octyl alcohol was isolated from this worm in comparatively large amounts and the presence of octanoic acid was suggested at that time.[5] Bacteriological investigation demonstrated the absence of anaerobic bacteria. Thus the marine tube worm appeared to be a suitable species for a study to determine if the acids found in the parasitic hog worm could be synthesized by this "anaerobic-bacteria-free" worm.

No five-carbon acids were found but the tube

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(1) E. Bueding and H. W. Yale, *J. Biol. Chem.*, **193**, 411 (1951).

(2) V. Moyle and E. Baldwin, *Biochem. J.*, **51**, 504 (1952).

(3) E. Bueding, *J. Biol. Chem.*, **202**, 505 (1953).

(4) W. Epps, M. Weiner and E. Bueding, *J. Infect. Dis.*, **87**, 149 (1950).

(5) D. R. Idler and U. H. M. Fagerlund, THIS JOURNAL, **75**, 6312 (1953).

worm apparently can synthesize formic, acetic, propionic and octanoic acids. The last named acid was not present in sufficient quantity to establish it definitely as *n*-octanoic acid at this time, but it is an octanoic acid and the presence of *n*-octyl alcohol is circumstantial evidence in favor of *n*-octanoic acid. The synthetic isomers of *n*-octanoic acid were not available for comparison with the acid from the tube worm. This acid could conceivably arise from *n*-octyl alcohol during isolation but because of the mild conditions employed and the failure of *n*-octyl alcohol to oxidize under similar conditions, this does not appear likely.

Although the function of *n*-octyl alcohol has still not been determined, the presence of octanoic acid suggests a role in fatty acid synthesis. It is pointed out, however, that the concentration of *n*-octyl alcohol is many times that of octanoic acid and the primary role of the alcohol in metabolism may be quite distinct from fatty acid synthesis.

Experimental

Isolation of Fatty Acids.—Ten kilograms of fresh tube worms was ground up in a large volume of water, the protein was precipitated with tungstic acid, and a clear solution was obtained by filtration through Celite. The residue was then resuspended in water and washed in this manner several times. Magnesium sulfate was added to the filtrate to give a final concentration of 25%. The filtrate was then distilled until magnesium sulfate began to crystallize out of the boiling solution. The distillate was neutralized with sodium hydroxide and concentrated to 300 ml. Neutral compounds (including *n*-octyl alcohol) were extracted with ether. The aqueous phase was then acidified with 10 *N* sulfuric acid, magnesium sulfate added to 25% concentration and the steam-volatile fatty acids were again distilled off. The distillate was neutralized with sodium hydroxide and concentrated to 5 ml. Excess potassium acid sulfate was added to liberate the free fatty acids from the sodium salts.

Determination of Fatty Acids.—Formic acid was determined by distilling an aliquot of the potassium acid sulfate solution with, and without, mercuric oxide.[6]

Another aliquot was taken for the determination of acetic and propionic acids. Distillation was carried out in the presence of mercuric oxide. The distillate was then neutralized with sodium hydroxide and the water removed *in vacuo*. The dry sodium salts were treated with 10 *N* sulfuric acid and the fatty acids were extracted with ether. The ether was then dried and any sulfuric acid was removed by passage through dry Celite. The acetic and propionic acids were then quantitatively separated on 20 g. of silicic acid previously treated with 17.5 ml. of methanol:water 10:4 containing 0.07 ml. of 2 *N* ammonium hydroxide and 0.5 ml. of a 1% methanolic solution of brom cresol green indicator using a chloroform developer saturated with the inside phase.[7] This showed the mixture to be composed of 65% acetic acid and 35% propionic acid. To confirm the presence of these acids a chromatogram employing authentic propionic and acetic acids was run and corresponded exactly to the unknown mixture. A larger chromatogram was then run and the Duclaux values were determined on the unknowns.

Anal. Duclaux values for acetic and propionic acids: 6.8, 7.1, 7.4; 11.9, 11.7, 11.3. Found: 6.9, 7.2, 7.4; 11.8, 11.7, 11.3.

The percentage of each acid as found chromatographically was then confirmed by means of the Duclaux values of the mixture and found to be 66% acetic acid and 34% propionic acid. The identity of the propionic acid was also confirmed by paper chromatography with a butanol:1.5 *N* ammonium hydroxide solvent.[8] Both the known and unknown acids had an R_f value of 0.20. As a final identification the *p*-toluidides of acetic (m.p. 153°) and propionic (m.p. 123°) acids from the tube worm were prepared. Neither melting point was depressed by the corresponding synthetic *p*-toluidide.

The octanoic acid was extracted from the potassium acid sulfate solution with low boiling petroleum ether and chromatographed on Celite with a methanol:petroleum ether solvent system.[7] The octanoic acid from the tube worm corresponded exactly to *n*-octanoic acid which was chromatographed on the same column after the tube worm acid had been eluted. The tube worm acid also behaved identically to *n*-octanoic acid on a butanol:1.5 *N* ammonium hydroxide paper chromatogram.[8] Both had an R_f value of 0.63.

The composition of the steam-volatile acids is shown in Table I.

TABLE I

STEAM-VOLATILE FATTY ACIDS OF *Eudistylia vancouveri*

Acids	Concn. in worm, mg./kg.	% of total volatile acids
Formic	27.0	11.5
Acetic	133.0	56.5
Propionic	71.5	30.5
Octanoic	3.4	1.5
Total	234.9	100

Acknowledgment.—We are indebted to Dr. H. L. A. Tarr and Miss B. A. Southcott for the bacteriological investigation.

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The Condensation of Acyclic Aldehydes with *p*-Nitrophenylacetic Acid. III. Crotonaldehyde, Methacrylaldehyde and Tiglaldehyde

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RECEIVED FEBRUARY 16, 1954

Conditions have been established by which acrolein[2] and several saturated aldehydes[3] may be condensed with *p*-nitrophenylacetic acid. It is the purpose here to extend the investigation to include crotonaldehyde, methacrylaldehyde and tiglaldehyde.

The condensations were effected by warming *p*-nitrophenylacetic acid with sodium acetate and the aldehyde in acetic anhydride solution, essentially the Oglialoro[2,4] modification of the Perkin condensation. Each aldehyde required a different reaction temperature and a different time for reaction for optimum yield: for crotonaldehyde, 18 hours at 63°; for methacrylaldehyde, 2 weeks at 37°; and for tiglaldehyde, 4 days at 63°. The generally observed decrease in yield with increased time and higher temperatures has been previously noted[2] and it required carrying out the condensations at relatively long times and at as low temperatures as were practicable to obtain reasonable yields of readily purified acids.

As with acrolein,[2] *p*-nitrotoluene, from decarboxylation of *p*-nitrophenylacetic acid, was isolated. No attempt was made to characterize vary-

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