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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[6] T. E. Friedemann, *J. Biol. Chem.*, **123**, 161 (1938).

[7] F. M. Strong, "Advanced Biochemical Technics," Laboratory Directions, Dept. of Biochemistry, Univ. of Wisconsin, Madison, revised 1949.

[8] F. Brown and L. P. Hall, *Nature*, **166**, 66 (1950).

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

BY H. J. GUNST,[1] M. TOBKES[1] AND ERNEST I. BECKER

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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[1] From the B.S. thesis of H. J. G. (1949), and the M.S. thesis of M. T. (1954).

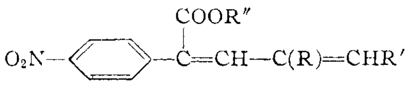
[2] G. W. Thielcke and E. I. Becker, *J. Org. Chem.*, **15**, 1241 (1950).

[3] W. H. Häffcke and E. I. Becker, *ibid.*, **16**, 863 (1951).

[4] J. R. Johnson in "Organic Reactions," Vol. I, Edited by R. Adams, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 221.

TABLE I

PHYSICAL PROPERTIES OF THE DIENOIC ACIDS AND THEIR ESTERS



$O_2N-C_6H_4-C(COOR'')=CH-C(R)=CHR'$

Compound					Empirical	Analyses, %							
						Neut. equiv.		Carbon		Hydrogen		Nitrogen	
No.	R	R′	R″	M.p., °C.	formula	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
I	H	CH_3	H	230–230.5 dec.	$C_{12}H_{11}NO_4$	233	233	61.80	61.67	4.76	4.92	6.01	5.96
II	CH_3	H	H	196–197 dec.	$C_{12}H_{11}NO_4$	233	234	61.80	61.62	4.76	4.81	6.01	6.00
III	CH_3	CH_3	H	177.5-178	$C_{13}H_{13}NO_4$	247	249	63.15	63.24	5.30	5.38	5.67	5.71
IV	H	CH_3	[a]	174	$C_{19}H_{16}N_2O_6$			61.95	62.20	4.38	4.60	7.61	7.59
V	CH_3	H	[a]	257.5–258.5 dec.	$C_{29}H_{16}N_2O_6$			61.95	62.24	4.38	4.54	7.61	7.53
VI	CH_3	CH_3	[a]	162.5	$C_{29}H_{18}N_2O_6$			62.82	63.06	4.74	4.80	7.33	7.44

[a] $R'' = -CH_2C_6H_4NO_2(p)$.

ing amounts of neutral, polymeric material which accompanied the *p*-nitrotoluene.

The acids were characterized as their *p*-nitrobenzyl esters (Table I) and by their pK_A's and ultraviolet absorption spectra (Table II). The pK_A's were obtained by measuring the *p*H's of the half-neutralized solutions of the acids.

TABLE II

pK_A'S AND ULTRAVIOLET ABSORPTION OF THE DIENOIC ACIDS[a]

Compound	pK_A	$\lambda_{max.}$, mμ	ε	Shoulder, $\lambda_{infl.}$	Inflections at ε
I	6.88	257.5	21,950	288	10,800
				356	2,300
II	4.40	280	10,350	..	....
III	6.10	260	18,250	283	12,100
p-Nitrophenylacetic acid	3.85[b]	270	10,000		
2-(4′-Nitrophenyl)-but-2-enoic acid[c]	5.00	282	9,600		

[a] For the general shape of these curves, see footnote 3. [b] J. F. J. Dippy and F. R. Williams, *J. Chem. Soc.*, 162 (1934). [c] Kindly furnished by W. H. Häffcke.

Several preliminary attempts to decarboxylate the acids with copper–quinoline to give the corresponding alkyl-*p*-nitrophenylbutadienes were unsuccessful.

Experimental[5]

2-(*p*-Nitrophenyl)-hexa-2,4-dienoic Acid (I).—The synthesis of this acid can also serve as a model for II.

p-Nitrophenylacetic acid (9.05 g., 0.05 mole) and 100 mg. of hydroquinone were dissolved in 25 ml. of warm acetic anhydride. Sodium acetate (4.10 g., 0.05 mole) was then added and followed by 5.0 ml. (4.3 g., 0.06 mole) of crotonaldehyde. Air was displaced by nitrogen and the reaction mixture was held at 63° for 16 hr. with intermittent shaking. At this time a mixture of 100 ml. of water and 25 ml. of hydrochloric acid was added and the contents were heated on a water-bath for 2 hr. After cooling, the contents were taken up in chloroform and washed with several portions of cold water, which were discarded. The organic layer was extracted with three 200-ml. portions of saturated sodium acid carbonate, which were combined and acidified to give an almost white precipitate which was washed with boiling water to leave 6.04 g. of crude acid. Recrystallization from ethanol (charcoal) gave 5.48 g. of pale yellow needles, m.p. 230–230.5° dec.

Evaporation of the chloroform solution gave 1.51 g. of a neutral reddish brown gum. Extraction of the hot water washes of the crude acid with chloroform and evaporation of the organic layer to dryness gave 1.44 g. (8.0 mmoles, 16%) of unreacted *p*-nitrophenylacetic acid, m.p. 143–152°.

4-Methyl-2-(*p*-nitrophenyl)-penta-2,4-dienoic Acid (III).—Because of the thermal instability of this compound it was necessary to carry out the condensation at a lower temperature and, therefore, for a longer time than the previously described acids. Otherwise, the reaction was set up as before using 0.05 mole of each of the reactants. At the end of the reaction period (two weeks at 37°) the reaction mixture was taken up in chloroform, transferred to a separatory funnel and washed with water slowly overnight by means of a gas diffuser tube placed at the bottom of the funnel and connected to a water tap and allowing the overflow to run into the drain. The chloroform solution was then extracted with three 250-ml. portions of saturated sodium acid carbonate. Acidification gave a precipitate which was dissolved in chloroform and stirred overnight with charcoal. After filtration hexane was added to incipient crystallization and the solution was cooled to −12° overnight. Filtration gave light yellow needles which, after washing several times with cold, peroxide-free ether, weighed 2.56 g. (0.011 mole, 22%) and melted 196–197° dec.

Characterization of the Acids.—The pure acids are unsaturated toward bromine in carbon tetrachloride and potassium permanganate in acetone.

The *p*-nitrobenzyl esters were prepared by the method of Shriner and Fuson[6] in yields of 56% (IV), 37% (V) and 25% (VI).

Attempted Decarboxylation of the Acids.—No pure diene was isolated in any of the experiments. A single attempt is described.

A mixture of 5.0 g. of I and 1.0 g. of copper powder was heated to 210° in quinoline with stirring and maintained at that temperature for 15 minutes. Evolution of carbon dioxide began at 185°. The reaction mixture was poured into 150 ml. of 10% hydrochloric acid, filtered, and the filter paper washed free of organic material with acetone. The filtrate was extracted with chloroform, and then the chloroform layer was washed successively with dilute hydrochloric acid, water, and saturated sodium acid carbonate solution, stirred with charcoal, filtered and distilled to dryness. The residue could not be induced to crystallize. Acidification of the sodium acid carbonate extract failed to precipitate any acid.

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[5] All temperatures are corrected. Analyses for carbon and hydrogen were carried out by Dr. K. Ritter, Basel, Switzerland; analyses for nitrogen by Mr. N. J. Alicino, Metuchen, New Jersey.

[6] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 157.

Identity of Some 1-(3′,4′-Dimethoxyphenyl)-6,7-dimethoxytetralin Derivatives

BY R. D. HAWORTH AND G. N. WALKER

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Several compounds recently reported by one of us (G. N. W.)[1,2] have been found to be identical with compounds prepared earlier.[3–5] Thus samples

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[1] G. N. Walker, THIS JOURNAL, **75**, 3387 (1953).

[2] G. N. Walker, *ibid.*, **75**, 3393 (1953).

[3] R. D. Haworth and G. Sheldrick, *J. Chem. Soc.*, 636 (1935).

[4] R. D. Haworth and D. Woodcock, *ibid.*, 813 (1938).

[5] R. D. Haworth and G. Sheldrick, *ibid.*, 291 (1941).