that the *l*-rhamnonic lactone which Will and Peters measured in 1889 was the 1,5- rather than the 1,4-lactone.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

PREPARATION AND BACTERIOLOGICAL ACTION TOWARD B. LEPRAE OF CERTAIN OLEFINIC ACIDS. XVII[1]

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Although the various cyclopentenyl alkyl acetic acids showed only slightly greater bactericidal action to *B. Leprae* than the corresponding cyclopentyl acids, a more careful study of the effects of an olefin linkage substituted in various dialkyl acetic acids has been undertaken. Representatives of three types of acids were prepared, allyl alkyl acetic acids, undecenyl alkyl acetic acids, and certain dialkyl acetic acids with the olefin linkage in the α,β-position. The bacteriological results are shown in Table I. The authors are indebted to Dr. W. M. Stanley for making these tests.

TABLE I

BACTERIOLOGICAL ACTION TOWARD *B. Leprae*

	Dilutions of sodium salts in thousands												
	5	15	25	50	62	74	85	100	125	155	192	250	330
Allyl alkyl acetic acids													
$C_3H_5CH(CO_2H)C_9H_{19}$-*n*	−	−	−	−	−	−	+	+	+	+	+	+	+
$C_3H_5CH(CO_2H)C_{10}H_{21}$-*n*	−	−	−	−	−	−	−	±	+	+	+	+	+
$C_3H_5CH(CO_2H)C_{11}H_{23}$-*n*	−	−	−	−	−	−	−	−	−	+	±	+	+
$C_3H_5CH(CO_2H)C_{12}H_{25}$-*n*	−	−	−	−	−	−	−	−	−	−	−	−	+
$C_3H_5CH(CO_2H)C_{13}H_{27}$-*n*	−	−	−	−	−	−	−	−	−	±	+	+	+
$C_3H_5CH(CO_2H)C_{14}H_{29}$-*n*	−	−	−	−	−	−	−	−	+	+	+	+	+
Undecenyl alkyl acetic acids													
$C_{11}H_{21}CH(CO_2H)C_4H_9$-*n*	−	−	−	−	−	−	−	−	−	−	−	+	+
$C_{11}H_{21}CH(CO_2H)C_5H_{11}$-*n*	−	−	−	−	−	−	±	±	±	−	±	±	+
$C_{11}H_{21}CH(CO_2H)C_6H_{13}$-*n*	−	−	−	−	±	±	±	+	+	+	±	+	+
$C_{11}H_{21}CH(CO_2H)C_7H_{15}$-*n*	−	−	−	±	+	±	±	+	+	+	+	+	+
α,β-Unsaturated acids													
$C_3H_7CH{=}C(CO_2H)C_4H_9$-*n*	−	+	+	+	+	+	+	+	+	+	+	+	+
$C_6H_{13}CH{=}C(CO_2H)C_7H_{15}$-*n*	−	−	−	−	−	−	−	−	−	−	−	±	+
$C_7H_{15}CH{=}C(CO_2H)C_8H_{17}$-*n*	−	−	−	−	−	−	−	−	−	−	+	+	+

By comparison of these data with those of the corresponding saturated acids containing the same number of carbon atoms[1b] it can be concluded that the presence of the olefin linkage has very little effect, if any, upon the bactericidal action. Moreover, the position of the olefin linkage in relation to the carboxyl appears to have no definite significance.

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[1] The previous two papers in this series are (a) Ford and Adams, XVI, THIS JOURNAL, **52,** 1259 (1930); (b) Stanley, Jay and Adams, XV, *ibid.*, **51,** 1261 (1929).

The allyl and undecenyl derivatives were made through the corresponding malonic esters. The α,β- unsaturated compounds were prepared by brominating the saturated acid, esterifying and then saponifying and eliminating hydrogen bromide.

Experimental

The details for preparing the proper halides, the substituted malonic esters and the monobasic acids can be found in the previous papers. The compounds containing the allyl and undecenyl groups were prepared by introducing the unsaturated groups second to the alkyl groups.

In producing the α,β-unsaturated acids, the acids were treated with bromine and phosphorus and the bromo acid bromides thus produced esterified directly with ethyl alcohol. The bromo esters were distilled under diminished pressure and then saponified with alcoholic potassium hydroxide.

α,β-Unsaturated Acids.—Organic acid (1 mole) was mixed with red phosphorus (0.33 mole) and bromine (1.8 mole) was run in slowly with vigorous stirring. After the initial reaction was over, the mixture was heated on a steam-bath for one-half to one hour. Upon cooling the separated material was filtered and absolute alcohol added slowly to the filtrate. After the reaction was over, the excess alcohol was removed on a steam-bath and the product washed with water, dried and distilled under diminished pressure. The ethyl α-bromo-di-*n*-heptyl acetate, b. p. 170–172° (2 mm.), ethyl α-bromo-di-*n*-butyl acetate, b. p. 102–104° (1.5 mm.), and ethyl α-bromo-di-*n*-octyl acetate, 179–181° (2 mm.), were obtained in this way.

A solution of 20% excess over two moles of potassium hydroxide dissolved in three to four times its weight of methyl alcohol was heated and the bromo ester slowly poured in. After several hours of refluxing the potassium bromide was filtered and most of the alcohol removed on a water pump. The potassium salt thus obtained was dissolved in water, steam was blown through to remove all alcohol and the solution then evaporated to dryness. Upon solution in water and pouring into excess hydrochloric acid, the free acid separated. It was extracted with ether, the ether removed and the acid purified by distillation under diminished pressure.

TABLE II

DIETHYL ALLYL ALKYL MALONATES

	B. p., °C.	n_D^{20}	d_4^{20}	Calculated, % C	Calculated, % H	Found, % C	Found, % H
$C_3H_5C(CO_2C_2H_5)_2C_9H_{19}$	144–146 (2 mm.)	1.4465	0.9469	69.88	10.50	69.21	10.43
$C_3H_5C(CO_2C_2H_5)_2C_{10}H_{21}$	154–155 (2.5 mm.)	1.4471	.9392	70.53	10.66	69.85	10.51
$C_3H_5C(CO_2C_2H_5)_2C_{11}H_{23}$	168–169 (5 mm.)	1.4478	.9345	71.18	10.73	71.10	10.61
$C_3H_5C(CO_2C_2H_5)_2C_{12}H_{25}$	166–168 (2.5 mm.)	1.4484	.9305	71.67	10.94	71.59	11.05
$C_3H_5C(CO_2C_2H_5)_2C_{13}H_{27}$	178–182 (5 mm.)	1.4499	.9276	72.19	11.07	72.04	10.91
$C_3H_5C(CO_2C_2H_5)_2C_{14}H_{29}$	184–186 (1.5 mm.)	1.4502	.9239	72.66	11.19	72.44	11.24

TABLE III

UNDECYLENYL ALKYL MALONIC ESTERS

	B. p., °C.	n_D^{20}	d_{20}^{20}	Calculated, % C	Calculated, % H	Found, % C	Found, % H
$C_{11}H_{21}C(CO_2C_2H_5)_2C_4H_9$	158–190 (4 mm.)	1.4501	0.9206	71.67	10.94	71.90	11.02
$C_{11}H_{21}C(CO_2C_2H_5)_2C_5H_{11}$	190–194 (4 mm.)	1.4530	.9344	72.18	11.07	72.20	11.00
$C_{11}H_{21}C(CO_2C_2H_5)_2C_6H_{13}$	207–209 (4 mm.)	1.4514	.9258	72.66	11.19	72.79	11.23
$C_{11}H_{21}C(CO_2C_2H_5)_2C_7H_{15}$	208–211 (4 mm.)	1.4518	.9225	73.10	11.29	73.00	11.12

TABLE IV

ALLYL ALKYL ACETIC ACIDS

	B. p., °C.	n_D^{20}	d_4^{20}	Calculated, %		Found, %	
				C	H	C	H
$C_3H_5CH(CO_2H)C_9H_{19}$	148–150 (3 mm.)	1.4510	0.9015	74.27	11.58	74.01	11.42
$C_3H_5CH(CO_2H)C_{10}H_{21}$	149–151 (1–1.5 mm.)	1.4520	.8989	74.93	11.75	74.75	11.38
$C_3H_5CH(CO_2H)C_{11}H_{23}$[a]	167–169 (4 mm.)	1.4530	.8953	75.69	11.81	75.30	11.78
$C_3H_5CH(CO_2H)C_{12}H_{25}$	164–166 (1–2 mm.)	1.4540	.8933	76.04	12.02	75.48	12.12
$C_3H_5CH(CO_2H)C_{13}H_{27}$[b]	179–183 (5 mm.)	1.4556	.8879	76.52	12.13	76.37	12.05
$C_3H_5CH(CO_2H)C_{14}H_{29}$	187–188 (2.5 mm.)	1.4538	.8865	76.95	12.24	77.11	12.37
	(M. p. 24°)	(at 25°)	(at 25°)				

[a] This acid and the necessary intermediates were prepared by Marion S. Jay.

[b] This acid and the necessary intermediates were prepared by Wendell M. Stanley.

TABLE V

UNDECYLENYL ALKYL ACETIC ACIDS

	B. p., °C.	n_D^{20}	d_{20}^{20}	Calculated, %		Found, %	
				C	H	C	H
$C_{11}H_{21}C(CO_2C_2H_5)_2C_4H_9$	175–180 (3 mm.)	1.4566	0.8929	76.04	12.02	76.23	11.96
$C_{11}H_{21}C(CO_2C_2H_5)_2C_5H_{11}$	186–190 (3 mm.)	1.4575	.8956	76.52	12.14	75.98	11.98
$C_{11}H_{21}C(CO_2C_2H_5)_2C_6H_{13}$	200–204 (3 mm.)	1.4564	.8915	76.95	12.24	76.87	12.17
$C_{11}H_{21}C(CO_2C_2H_5)_2C_7H_{15}$	205–209 (5 mm.)	1.4572	.8870	77.34	12.34	77.23	12.38

TABLE VI

α,β-UNSATURATED DIALKYL ACETIC ACIDS

	B. p., °C.	n_D^{20}	d_{20}^{20}	Calculated, %		Found, %	
				C	H	C	H
$C_4H_9C(CO_2H)CHC_3H_7$	121–123 (2 mm.)	1.4484	0.9456	70.53	11.67	67.80	11.24
$C_7H_{15}C(CO_2H)CHC_6H_{13}$	180–182 (2 mm.)	1.4566	.8993	75.52	11.89	74.49	12.12
$C_8H_{17}C(CO_2H)CHC_7H_{15}$	185–186 (1 mm.)	1.4625	.8983	76.51	12.12	75.95	12.08

Summary

Various allyl alkyl acetic acids, undecenyl alkyl acetic acids and α,β-unsaturated acids have been prepared and tested for bactericidal action to *B. Leprae*. The unsaturated acids appear to be of about the same bactericidal value as the corresponding saturated acids.

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