growth when an essential nutrilite is omitted, but on addition of this nutrilite maximal growth response should be observed.

The medium shown in Table I was adapted for use in this investigation. It is essentially the same as media previously reported[1-6] with the exception that thiamin and folic acid[7] have been added, thereby making the medium complete nutritionally for both *L. casei* and *L. arabinosus 17-5*. Thiamin acts as a stimulatory factor for the nutrition of *L. casei*, whereas folic acid stimulates the growth of *L. arabinosus*.

Table II demonstrates that maximal growth response is not obtained when previously proposed media for *L. casei*[5] or *L. arabinosus*[1] are employed. When casein hydrolyzate supplemented with cystine and tryptophan replaced the synthetic amino acids as the source of nitrogen, 90–95% of the maximal growth occurred. The medium *L. casei*[5] supported a growth response of 60 to 70% which was increased by the addition of thiamin to 90 to 95%, whereas folic acid increased the growth response of *L. arabinosus*[1] from 70 to 80% to 90 to 95%.

TABLE II

GROWTH RESPONSE OF *L. Casei* AND *L. Arabinosus* 17-5 IN VARIOUS CULTURE MEDIA

Medium	Amount of 0.1 *N* alkali required to neutralize 10 ml. medium after seventy-two hours of incubation: *L. casei* ml.	*L. arabinosus* ml.
1. Hutchings and Peterson[a]	7–8[b]	
2. Hutchings and Peterson[a] amino acids replaced by casein hydrolyzate supplemented with tryptophan and cystine	10–10.5	
3. Shankman[1]		7– 8.5
4. Shankman,[1] amino acids replaced with casein hydrolyzate supplemented with tryptophan and cystine		10–10.5
5. Proposed medium: 2 mg. each of 20 amino acids per tube	10–10.5	10–10.5
6. Same as No. 5, thiamin omitted	7–8	
7. Same as No. 5, folic acid omitted		8–9

[a] 1% glucose and 0.6% anhydrous sodium acetate used. [b] Theoretical acid production corresponds to 11.1 ml. of 0.1 *N* NaOH.

When the medium outlined in Table I was used in amino acid assays, no appreciable growth occurred when an essential amino acid was omitted (Blank titration values of 0.7 to 2.0 ml. of 0.1 *N* alkali). When the same essential amino acid was added in the proper concentration, maximal growth response was obtained.

(7) B. L. Hutchings, N. Bohonos and W. H. Peterson, *J. Biol. Chem.*, **141**, 521 (1941).

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Xylitol Esters of Fatty Acids

BY J. F. CARSON, JR., AND W. D. MACLAY

A series of fatty acid esters of the pentahydric alcohol, xylitol, has been prepared in connection with a study of plasticizers. The only esters of xylitol recorded in the literature are the pentaacetate[1] and the pentanitrate.[2]

Xylitol was prepared by high-pressure catalytic hydrogenation of D-xylose. The esters, xylitol pentapropionate, pentabutyrate, pentalaurate, pentamyristate, pentapalmitate, and pentastearate, were prepared by reaction of xylitol with the corresponding acid anhydride or acid chloride in pyridine. Xylitol pentapropionate and pentabutyrate are oily liquids with interesting possibilities as plasticizers for cellulose esters.[3] The xylitol penta-esters of lauric, myristic, palmitic and stearic acids are low-melting waxy solids. These latter esters could not be saponified completely with the customary ethanol–potassium hydroxide reagent; after refluxing for six hours, hydrolysis was only 50% complete. Saponification with a solution of potassium hydroxide in *n*-butyl alcohol for two hours gave satisfactory saponification equivalents. Data on the new xylitol esters are recorded in Table I.

TABLE I

PHYSICAL AND CHEMICAL CONSTANTS OF XYLITOL ESTERS

Ester, xylitol	M. p., °C.	d^{25}_4	$n^{25}D$	Saponification equivalent: Calcd.	Found
Pentapropionate	.....	1.1176	1.4424	86.4	86.8
Pentabutyrate	.....	1.0606	1.4436	100.4	100.1
Pentalaurate	33.5–35	....	....	213	214
Pentamyristate	45.5–47	....	....	241	239
Pentapalmitate	56–58	....	....	269	270
Pentastearate	66–68	....	....	297	295

Experimental

Preparation of Xylitol Pentapropionate and Pentabutyrate.—These esters were prepared by reaction of 15.0 g. (0.099 mole) of dry xylitol with 0.61 mole of the corresponding anhydride in 100 g. of pyridine. The reaction mixture was heated on a steam-bath for three hours and the ester isolated as an oil on pouring into a liter of chopped ice. The aqueous mixture was extracted with benzene or toluene, and the extract was washed successively with 3% sodium carbonate solution, 3% hydrochloric acid, and distilled water. Removal of the solvent *in vacuo* yielded the esters as pale amber liquids in 90–95% yields. Xylitol pentapropionate and pentabutyrate were purified by evaporative distillation in a short-path still of a type described by Matchett and Levine[4] at 0.1 mm. and a bath temperature of 120–150°. The distillations proceeded without noticeable decomposition to give almost quantitative yields of colorless product.

(1) Hockett and Hudson, THIS JOURNAL, **57**, 1753 (1935).
(2) Bertrand, *Bull. soc. chim.*, [3] **5**, 556, 740 (1891).
(3) Elam, Preusser and Page, *Modern Plastics*, **20**, No. 9, 95 (1943).
(4) J. R. Matchett and J. Levine, *Ind. Eng. Chem., Anal. Ed.*, **15**, 296 (1943).

Anal. for xylitol pentapropionate: Calcd. for $C_{20}H_{32}O_{10}$: C, 55.54; H, 7.46. Found: C, 55.2; H, 7.44.

Anal. for xylitol pentabutyrate: Calcd. for $C_{25}H_{42}O_{10}$: C, 59.74; H, 8.42. Found: C, 59.5; H, 8.38.

Preparation of Xylitol Pentalaurate, Pentamyristate, Pentapalmitate, and Pentastearate.—These esters were prepared by reaction of xylitol with the appropriate acid chloride in the presence of pyridine. The acid chlorides were prepared by the method of Ralston[5] from Eastman acids.

To a solution of 5.0 g. (0.033 mole) of xylitol in 150 g. of dry pyridine, 0.2 mole of acid chloride was added in small portions at a time and the reaction mixture was heated on a steam-bath for four hours under anhydrous conditions. The mixture was extracted with toluene and the toluene extract was washed successively with 3% potassium hydroxide, 3% hydrochloric acid, and distilled water. The extract was decolorized with carbon, and the solvent was removed *in vacuo*, yielding the ester as a solid residue. Yields of 88, 84, 95, and 95% were obtained for the pentalaurate, pentamyristate, pentapalmitate and pentastearate, respectively. Xylitol pentalaurate and pentamyristate were most conveniently purified by recrystallization from 4 parts of acetone at −15°. The palmitic and stearic acid esters were conveniently recrystallized from acetone or toluene at −20°.

(5) Ralston, THIS JOURNAL, **61**, 1019 (1939).

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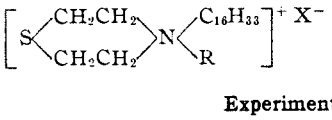
Invert Soaps. Thiomorpholinium Salts[1]

BY WILLIAM F. HART AND JOSEPH B. NIEDERL

Studies of the morpholine types of "invert soaps"[2] have been extended to the corresponding sulfur analogs. Recognizing the importance of a "cetyl" group in bacteridical "invert soaps"[3] N-cetylthiomorpholine was studied first. This compound was prepared by condensing cetylamine with mustard gas utilizing the methods of H. T. Clarke[4] and W. E. Lawson and E. E. Reid[5] as follows:

$$C_{16}H_{33}NH_2 + (ClCH_2CH_2)_2S \xrightarrow[C_2H_5OH]{\Delta\ Na_2CO_3} S<(CH_2CH_2)_2>NC_{16}H_{33}$$

The above tertiary amine upon treatment with appropriate alkyl halides and sulfates was then converted into the respective quaternary thiomorpholinium salts of the "simple invert soaps" types:



R: methyl, ethyl, propyl, benzyl
X: Cl, Br, I, CH_3SO_4-, $C_2H_5SO_4$-

Experimental

N-Cetylthiomorpholine.—Seventy-six grams of cetylamine (b. p. 325° uncor.) was dissolved in 120 ml. of absolute alcohol and 34 g. of anhydrous sodium carbonate added. Fifty grams of mustard gas was then added, and the solution was refluxed for eight hours. The warm solution was filtered to remove inorganic salts, which were washed twice with hot absolute alcohol. The combined alcohol extracts were distilled *in vacuo* to remove the solvent. The residue was then taken up in an excess of dry ether, and saturated with dry hydrogen chloride. The hydrochloride was filtered off and washed repeatedly with dry ether and with acetone. The free base was obtained by taking up the hydrochloride in a concentrated potassium hydroxide solution and extracting with ether. The combined ether extracts were dried over solid potassium hydroxide pellets, and the solvent removed by distillation. The free base was purified by recrystallization from ether.

The picrate was prepared by adding an equal volume of a saturated aqueous solution of picric acid to an aqueous solution of the hydrochloride. This was purified by one recrystallization from alcohol.

Quaternary Thiomorpholinium Salts.—The methiodide and ethiodide were prepared by refluxing N-cetylthiomorpholine the free base with a slight excess of methyl and ethyl iodide, respectively, for three hours, allowing the excess alkyl iodide to evaporate spontaneously at the end of that period. The products were then taken up in warm ethyl acetate in which thiothiomorpholinium iodides are soluble, cooled, filtered, and recrystallized from the same solvent.

The *n*-propyl bromide and benzyl chloride quaternary salts were prepared by refluxing the free base with an equivalent amount of the alkyl halide in toluene solution for six hours, distilling the solvent *in vacuo*, washing with dry acetone, and finally recrystallizing from ethyl acetate.

The alkyl sulfates were prepared by refluxing for four hours equivalent quantities of the free base and the respective di-alkyl sulfates, dimethyl and diethyl sulfate, in half the total volume of dry benzene.

TABLE I

Compound	Formula	M. p., °C. (uncor.)	Analyses, % N Calcd.	Found
N-Cetylthiomorpholine	$C_{20}H_{41}NS$	78	4.27	4.35
Hydrochloride	$C_{20}H_{42}NSCl$	162	3.82	3.93
Picrate	$C_{26}H_{44}O_7N_4S$	112	10.06	10.15
Methiodide	$C_{21}H_{44}NSI$	244	2.98	3.05
Ethiodide	$C_{22}H_{46}NSI$	205	2.90	3.02
n-Propyl bromide	$C_{23}H_{48}NSBr$	173	3.10	3.13
Benzyl chloride	$C_{27}H_{43}NSCl$	166	3.08	3.12
Methosulfate	$C_{27}H_{47}NS_2O_4$	210 dec.	3.08	3.15
Ethosulfate	$C_{24}H_{51}NS_2O_4$	Oil	2.90	2.97

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(1) Presented before the Division of Organic Chemistry at the New York City meeting of the American Chemical Society, September, 1944.

(2) J. B. Niederl and co-workers, THIS JOURNAL, **63**, 1476 (1941); **66**, 840 (1944).

(3) R. Kuhn, *Ber.*, **73**, 1080, 1095, 1100, 1105, 1109 (1940).

(4) H. T. Clarke, *J. Chem. Soc.*, **101**, 1583 (1912).

(5) W. E. Lawson and E. E. Reid, THIS JOURNAL, **47**, 2821 (1925).

The Preparation of the Trityl Ether of Propylene Glycol

BY NANCY GREEN AND MELVIN W. GREEN

During recent years, propylene glycol has been introduced into many types of pharmaceutical preparations and in fact standards governing its purity have been introduced into the National