[Contribution from the Northern Regional Research Laboratory[1]]

Esters of 1,4,7-Trihydroxyalkanes

By Charles R. Russell, Herbert E. Smith, L. S. Hafner and L. E. Schniepp

Received August 4, 1952

Esters of 1,4,7-heptanetriol, 1,4,7-octanetriol and 1-tetrahydrofuryl-3,6,9-nonanetriol with the even-numbered fatty acids from C_2 to C_{10} have been prepared. Properties of the purified products are reported.

The conversion of furfural condensation products to trihydroxyalkanes has recently been reported.[2] This paper is a continuation of a program of preparing new chemicals from furfural derivatives and describes the preparation and properties of a number of esters of 1,4,7-heptanetriol, 1,4,7-octanetriol and 1-tetrahydrofuryl-3,6,9-nonanetriol. Those properties of these esters which are of importance to their possible use as synthetic lubricants will be reported elsewhere.

The esters of these triols with even-numbered fatty acids from C_2 to C_{10}, with the exception of the heptanetriol triacetate, were prepared by heating the reactants, dissolved in benzene, in the presence of a catalytic amount of *p*-toluenesulfonic acid and removing the water of reaction. The pelargonate esters of heptanetriol and of tetrahydrofurylnonanetriol were prepared in the same manner.

Separation of the pure triesters from the small amounts of mono- and diesters in the crude reaction mixtures proved to be rather difficult. Purification was accomplished by various combinations of extractions and distillations. The distillations were done in alembic flask stills and in a falling-film type molecular still operated at low pressures. These methods and the order in which they were applied are indicated in the table.

Several alternative methods of esterification were investigated to determine their applicability to the preparation of triol esters. Octanetriol tributyrate was prepared by ester interchange, using isopropyl butyrate according to the method of Lippencott and Westfield.[3] The reaction was not complete and the product separation problem was still encountered. The procedure of Morgan,[4] using the acid anhydride and trifluoroacetic acid as the catalyst, was also tried on octanetriol with butyric anhydride. The reaction failed to go to completion in 16 hours.

Attempts to prepare the tricrotonate and the tribenzoate of 1-tetrahydrofuryl-3,6,9-nonanetriol were unsuccessful. In both cases the reaction, as indicated by water evolution, was very slow. The only pure product isolated from the crotonic acid reaction analyzed correctly for the dicrotonate of the triol. The benzoic acid reaction gave a product which analyzed for a monobenzoate of a dehydration product such as would be obtained if ring closure with formation of a second tetrahydrofuryl group occurred. This type of reaction would be expected to occur to some extent in all cases where triols of this general structure are heated in the presence of an acid catalyst.[2] The laurate, myristate, palmitate, stearate and oleate esters of 1-tetrahydrofuryl-3,6,9-nonanetriol and of 1,4,7-octanetriol were also prepared. All of these, except the oleates, were waxy solids. Since analytically pure samples were not obtained, no data relative to these compounds are being reported.

Experimental

Preparation of Esters. General Procedure.—From 0.3–0.5 mole of the respective triols and an excess of the acids indicated in the table were dissolved in 200 ml. of benzene and 2 g. of *p*-toluenesulfonic acid added. The reaction mixture was heated to reflux and the course of the reaction followed by the rate of water collection in a separating device attached between the flask and the reflux condenser. When water collection ceased the reaction mixture was cooled and 400 ml. more solvent was added. The solution was extracted with cold aqueous 5% sodium hydroxide in an amount slightly less than that calculated as necessary to neutralize the catalyst and excess acid. The remaining acid was removed by extraction with 10% sodium bicarbonate solution. The benzene layer was washed to neutrality with distilled water and then dried over anhydrous magnesium sulfate.

With the products from the higher molecular weight fatty acids it was necessary to add some *n*-butanol to break up emulsions and facilitate removal of the soaps which formed during these extraction operations.

The dry benzene solutions were filtered and the solvent removed by distillation on a steam-bath. Last traces of solvent and low boiling impurities were removed by heating on a steam-bath under reduced pressure. The crude esters were purified by the methods indicated in the table. The yields shown in the table for the once distilled esters are probably 10+% low because of the large holdup in the falling-film type molecular still.

Purification Methods.—The once distilled esters were reprocessed as necessary to bring their physical properties to a state of constancy and the analytical data into accord with calculated values. These purification steps and the order in which they were applied are indicated in the table. Since handling losses were quite high in these purification operations, no attempt was made to present yield data on the highly purified products.

Distillation.—Two types of apparatus were used for the purification of these products by distillation. Most of the esters were distilled at least once in a falling-film type molecular still equipped with a magnetically operated pumping device for recycling undistilled material. This still was also fitted with a fraction cutter which permitted the collection of three fractions without interrupting the course of the distillation. The still unit was attached to a manifold which was connected to a mercury vapor pump backed by an efficient mechanical pump. All samples were degassed at 125° at 10 to 50 μ for 1 hour before transferring them to this still.

The second type of apparatus was an alembic flask still similar in design to the still described by Cowan, Falkenburg and Teeter.[5] This still was operated with the boiler completely immersed in an electrically heated oil-bath. A very fine capillary extending to the bottom of the boiler prevented bumping. The use of a fraction cutter permitted the collection of up to five fractions without interrupting the distillation. In addition to its use for complete distillation

---

[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] C. R. Russell, K. Alexander, W. O. Erickson, L. S. Hafner and L. E. Schniepp, This Journal, **74**, 4543 (1952).

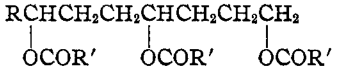
[3] S. B. Lippencott and N. J. Westfield, U. S. Patent 2,476,052 (1949).

[4] P. W. Morgan, *Ind. Eng. Chem.*, **43**, 2575 (1951).

[5] J. C. Cowan, L. B. Falkenburg and H. M. Teeter, *Ind. Eng. Chem., Anal. Ed.*, **16**, 50 (1944).

TABLE I

ESTERS OF 1,4,7-TRIHYDROXYALKANES



$$\underset{\displaystyle OCOR'}{RCH}CH_2CH_2\underset{\displaystyle OCOR'}{CH}CH_2CH_2\underset{\displaystyle OCOR'}{CH_2}$$

				Properties of purified esters										
R	R′	Yield,[a] %	Purification method	Dist. °C.	/μ Hg.[b]	n^{25}_D	d^{20}_4[c]	Sapn. equiv. Calcd.	Sapn. equiv. Found	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
H	CH_3[d]	30	*e*	75	4.0	1.4400	1.067	91.4	91.4	$C_{13}H_{22}O_6$	56.91	56.7	8.08	8.00
H	C_2H_5	74[f]	*e,e*	80	1.8	1.4420	1.021	105.5	107.7	$C_{16}H_{28}O_6$	60.73	60.8	8.91	8.94
H	C_3H_7	70	*e*	90	0.6	1.4433	0.991	119.5	121.4	$C_{19}H_{34}O_6$	63.63	63.8	9.55	9.58
H	C_5H_{11}	56	*e*	150	.5	1.4479	.950	147.5	149.3	$C_{25}H_{46}O_6$	67.83	67.9	10.47	10.35
H	C_7H_{15}	66	*e*	150	.7	1.4514	.931	175.6	176.5	$C_{31}H_{58}O_6$	70.67	70.8	11.09	10.80
H	C_8H_{17}	51	*e*	190	1.8	1.4530	.924	189.7	188.5	$C_{34}H_{64}O_6$	71.78	71.4	11.34	11.25
H	C_9H_{19}	59	*e*	200	1	1.4540	.915	203.6	203.0	$C_{37}H_{70}O_6$	72.90	72.6	11.55	11.55
CH_3	CH_3[k]	60	*f*	97	30	1.4387	1.044	96.1	96.7	$C_{14}H_{24}O_6$	58.31	58.4	8.39	8.36
CH_3	C_2H_5	51	*f*	110	20	1.4402	1.013	110.1	112.3	$C_{17}H_{30}O_6$	61.79	61.5	9.15	9.28
CH_3	C_3H_7	60	*f*	130	20	1.4414	0.984	124.1	126.6	$C_{20}H_{36}O_6$	64.48	64.1	9.74	9.82
CH_3	C_5H_{11}	58	*f,e*	140	5	1.4457	.952	152.2	151.8	$C_{26}H_{48}O_6$	68.36	68.4	10.59	10.76
CH_3	C_7H_{15}	55	*g,e,i,g,e*	175	2	1.4503	.927	180.3	184.2	$C_{32}H_{60}O_6$	71.06	70.9	11.18	11.36
CH_3	C_9H_{19}	56	*e*	210	2	1.4522	.923	208.3	208.1	$C_{38}H_{72}O_6$	73.01	73.0	11.61	11.67
THFE[l]	CH_3	64	*f*	157	20	1.4568	1.068	124.1	123.4	$C_{19}H_{32}O_7$	61.26	61.3	8.66	8.79
THFE	C_2H_5	63	*e,f*	175	40	1.4566	1.040	138.2	139.0	$C_{22}H_{38}O_7$	63.74	63.5	9.24	9.45
THFE	C_3H_7	66	*h,e*	150	4	1.4558	1.008	152.2	153.8	$C_{25}H_{44}O_7$	65.75	65.9	9.71	9.81
THFE	C_5H_{11}	56	*g,e*	180	5	1.4573	0.983	180.3	182.3	$C_{31}H_{56}O_7$	68.83	68.5	10.43	10.28
THFE	C_7H_{15}	54	*g,e,i,e*	200	2	1.4596	.954	208.3	211.0	$C_{37}H_{68}O_7$	71.10	71.2	10.96	10.96
THFE	C_8H_{17}	42	*g,e*	210	5	1.4606	.950	222.3	221.6	$C_{40}H_{74}O_7$	72.02	71.6	11.18	10.87
THFE	C_9H_{19}	55	*g,e,j,e*	200	2	1.4607	.947	236.3	236.3	$C_{43}H_{80}O_7$	72.83	72.7	11.37	11.46
THFE	C_3H_5[m]	27	*e*	175	5	1.4880	1.065	191.2	190.8	$C_{21}H_{34}O_6$	65.88	66.1	8.95	8.83
THFE	C_6H_5[n]	43	*f*	169	5	1.5115	1.052	332.5	331.0	$C_{20}H_{28}O_4$	72.25	71.6	8.51	8.42

[a] Calculated on the basis of the once-distilled product having an analytical purity of 95+%. All distillations except *d* and *f* were carried out on the falling-film still. [b] Observed on final distillation; temperature of the hot finger of the falling-film still; vapor temperature in alembic flask still. Pressure was measured by McLeod and calibrated thermocouple gages attached between still and solid CO_2-cooled trap. [c] Measured by Fischer–Davidson Gravitometer. [d] Prepared from tetrahydrofurylpropanol by method of A. Hinz, G. Meyer and G. Schucking, PB report 52020, page 1051 (*C. A.*, **41**, 6559 (1947). [e] Distilled in falling-film molecular still. [f] Distilled in alembic flask still. [g] Stripped of low-boiling impurities in alembic flask still. [h] Heptane solution extracted with 60% aqueous ethanol. [i] Heptane solution extracted with 85% aqueous ethanol. [j] Heptane solution extracted with 90% aqueous ethanol. [k] Previously reported. See reference *d*. [l] Tetrahydrofurylethyl = $\underbrace{(CH_2)_3CH}_{O}CH_2CH_2$–. [m] Data in accord with a dicrotonate ester. [n] Data in accord with a monobenzoate of a dehydration product corresponding in molecular weight to 1,5-ditetrahydrofurylpentanol-3.

of some esters, this still was also used for stripping out traces of acids and other low boiling impurities prior to distillation in the falling-film molecular still. This was done by heating the material in the still under high vacuum to a temperature just below the boiling point or, for the higher boiling esters, to a bath temperature of 200°. These conditions were maintained until no more volatile materials were collected.

Extraction.—In several cases the complete removal of mono- and diesters could not be accomplished by distillation alone. These impure esters were dissolved in heptane and the heptane solutions extracted several times with various concentrations of aqueous ethanol. Such extractions are indicated in the table.

Acknowledgment.—The authors wish to acknowledge the assistance of microanalysts, C. H. Van Etten and Mary B. Wiele, who performed all of the carbon and hydrogen analyses and determined many of the saponification equivalents.

PEORIA, ILLINOIS