acidity measured. These data of initial free acidity and also the results of hydrolysis at 100° and at 40° C. are shown in Table I.

The qualitative solubilities of some resins and gums in levulinic acid esters have been observed by treating approximately 0.5 gram of the substance with the 5-cc. portions of the esters. As these solubilities are similar for each group of isomers, the esters (Table II) are grouped in their respective series—methyl, ethyl, the propyl (C_3), butyl (C_4), and amyl (C_5) esters.

TABLE II. QUALITATIVE SOLUBILITY OF COMMERCIAL GUMS AND RESINS IN THE ESTERS OF LEVULINIC ACID

RESIN	METHYL[a]	ETHYL	C_3	C_4	C_5
x-Manila	−	−	−	×	×
Montol	×	+	+	+	+
Kauri	×	×	−	×	×
Pontianac chips	×	×	−	−	−
Rosin	+	+	+	+	+
Bone-dry shellac	−	−	−	−	−
Bakelite (viscous)	Gels	Gels	+	+	+
Rezyl	−	+	+	+	+
Sarpee	−	−	−	−	−
Ester gum, unoxidized	+	+	+	+	+
Ester gum, oxidized	×	+	+	+	+
Albertol copal	×	+	+	+	+
Albertol	×	+	+	+	+
Amberol	×	×	+	+	+
Cumar	+	+	+	+	+
Dammar	−	−	−	−	×
Varnish type glyptal	+	+	+	×	+
Vinylite 80	Gels	Gels	Gels	Gels	Gels
Urea formaldehyde	−	−	−	−	−

[a] + = completely soluble; − = insoluble; × = partially soluble.

In general, it was found that the esters are completely miscible with the simple alcohols, immiscible with ethylene glycol and glycerol, and miscible with ethers, aldehydes, ketones, esters, acids, chlorinated aliphatic hydrocarbons, aromatic hydrocarbons, the Cellosolve group, and fatty oils. Methyl levulinate differs from the above generalization in being completely miscible with ethylene glycol and immiscible with fatty oils. Ethyl levulinate is also immiscible with ethylene glycol.

The tolerance of levulinic acid ester solutions of 1/2 second nitrocellulose for dilution with (1) toluene, (2) *N*-butyl alcohol, and (3) Kemsoline (a commercial petroleum-distillate diluent) have been determined by the Hercules Powder Company's method for dilution ratios (*3*). These data are given in Table III.

TABLE III. DILUTION RATIOS OF SOLUTIONS OF 1/2 SECOND NITROCELLULOSE

ALKYL LEVULINATE	TOLUENE		BUTYL ALCOHOL		KEMSOLINE	
	Diln. ratio	% Nitrocellulose	Diln. ratio	% Nitrocellulose	Diln. ratio	% Nitrocellulose
Methyl	2.40	7.8	2.35	8.2	Immiscible	
Ethyl	2.85	7.2	3.25	7.4	0.45	6.9
N-propyl	3.00	7.3	3.85	8.0	0.75	5.9
Isopropyl	2.80	7.8	5.05	6.1	0.60	6.3
N-butyl	3.15	7.7	6.40	6.4	1.0	5.3
Isobutyl	2.95	8.0	6.00	6.8	0.85	5.6
sec-Butyl	2.75	7.7	5.55	6.5	0.85	5.7
N-amyl	3.25	7.4	7.50	7.2	1.15	5.1
Isoamyl	3.00	8.2	7.50	7.6	1.0	5.3
Methylpropylcarbinol	2.80	9.7	7.75	6.5	0.93	5.5
Diethylcarbinol	3.10	7.9	8.00	6.5	0.85	5.6
2-Methylbutyl	3.00	8.0	7.85	7.5	1.0	5.3
Mixed amyl	2.80	8.0	7.25	7.5	1.1	5.0

DISCUSSION OF RESULTS

An examination of the various data pertaining to the properties of the esters of levulinic acid reveals that the better characteristics for most present commercial uses of such materials are found in the members of the butyl and amyl series. Generally these esters are more stable toward water, have lower solubility relations to water, and better dilution ratios of nitrocellulose solutions than the lower homologs. Their solvent powers seem to be as good as those of the lower esters.

LITERATURE CITED

(1) Cowley and Schuette, *J. Am. Chem. Soc.*, **55**, 387 (1933).
(2) Cox and Dodds, *Ibid.*, **55**, 3391 (1933).
(3) Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers, Color," 5th ed., p. 730, Institute of Paint and Varnish Research, Washington, 1930.
(4) Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).
(5) Sah and Ma, *J. Am. Chem. Soc.*, **52**, 4880 (1930).
(6) Schuette and Cowley, *Ibid.*, **53**, 3485 (1931).
(7) Thomas and Schuette, *Ibid.*, **53**, 2324 (1931).

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III. Technology of Sucrose Octaäcetate and Homologous Esters

GERALD J. COX, JOHN H. FERGUSON, AND MARY L. DODDS

A simplified convenient method for the preparation of sucrose octaäcetate in high yield is described, together with analogous processes for making sucrose octapropionate and sucrose octabutyrate. Properties of value in the industrial application of these esters of sucrose are given.

THE fact that sucrose has been considered primarily as a food, condiment, or confection by the layman, or as an example of an abundant disaccharide by the chemist, has in most cases far overshadowed its possible use as a polyhydric alcohol. The production of esters from this compound, utilizing as it does these same alcoholic properties, therefore seemed to offer a starting point for the development of a group of industrially useful organic products.

The comparatively low cost and high available tonnage of sucrose obtainable in such a high state of purity as is commonly found upon the consumer's table also contributed to the belief that such a source material or some of its derivatives could be used both extensively and advantageously in industrial processes.

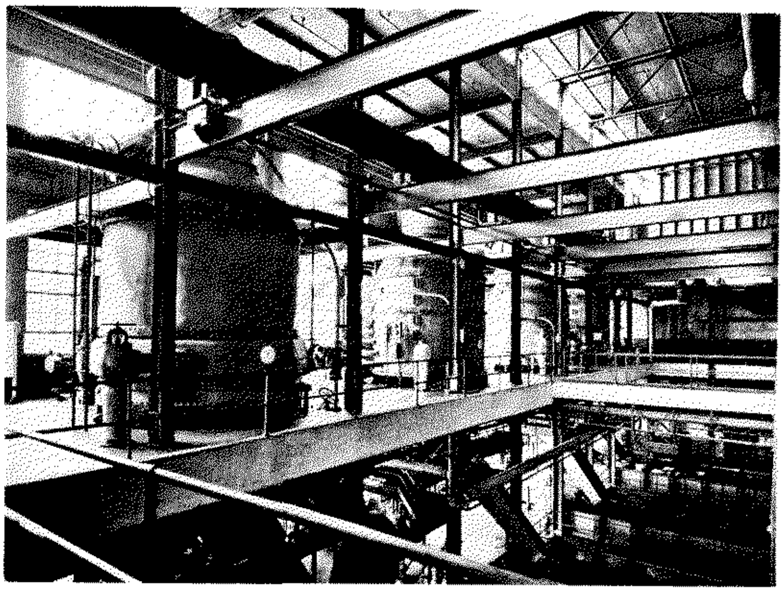
With this idea in mind, and cognizant of the extensive commercial use of the esters of allied substances—for example, cellulose acetate—the lower saturated aliphatic acids were considered as possible reactants for the production of similar compounds of sucrose.

The investigation to be reported, therefore, is concerned with some of the phases of production of the most promising member of the series—i. e., sucrose octaäcetate—together with the properties that might apply commercially to its use. Mention is also made of the properties of the two next highest members of the homologous series—i. e., sucrose octapropionate and sucrose octabutyrate.

Schutzenberger (*3*) was the first to acetylate sucrose but was able to obtain only a gummy mass from the process. Later Herzfeld (*1*) was able to obtain a crystalline product and likewise listed some of its physical characteristics. The octapropionate and octabutyrate are new compounds.

SUCROSE OCTAÄCETATE

LARGE-SCALE LABORATORY PRODUCTION IN GLASS. The preparation of sucrose octaäcetate in 6- to 8-pound lots was carried out, using the apparatus shown in Figure 1.



Refinery Pan Floor

The Liebig condenser, *A*, is ground into the neck of a 12-liter balloon flask, *B*. Through the 2-inch (5-cm.) condenser runs sleeve *C*, carrying stirrer *D* turned by motor *E* through the rubber-tube universal joint, *F*. The sleeve is made of heavy glass (4-mm. wall), braced at *G* with three glass points, and supported at *H* by a clamp and rubber stopper. The flask is heated by oil bath *J* and electric plate *K*.

Four thousand grams of commercial acetic anhyride (90 per cent) and 150 grams of freshly fused sodium acetate were placed in the 12-liter flask and heated to boiling with stirring (145° C. oil-bath temperature). The electric plate was shut off as the reaction was rapid and exothermic. Fifteen hundred grams of granulated sucrose were added down the condenser at the rate of about 100 grams per minute. After all the sucrose had been added, the electric plate was again turned on to continue rapid boiling of the reaction mixture. More acetic anhydride (500 grams) was poured down the condenser to wash into the reaction vessel any sucrose that had adhered to the sides. Boiling of the mixture was then continued for 10 minutes and the current again shut off. When refluxing ceased (in about 15 minutes) the solution was heated with 75 grams of decolorizing carbon (Nuchar) and filtered while hot into a 12-liter flask. The solution was evaporated *in vacuo* in a boiling water bath until the distillate came over only in occasional drops. The hot sirup was poured into about 12 liters of tap water contained in a 24-liter stoneware jar and stirred vigorously with a heavy paddle. The water was poured off and renewed, and stirring was continued until the sucrose acetate became a stiff mass. By allowing this mass to stand overnight in water, it became crystalline.

After the crystallization, the water was poured off and the hard mass was broken and ground in a mortar. It was then washed with tap water on a 12-inch (30.5-cm.) stoneware vacuum filter until the washings were entirely neutral to litmus paper. The final product was then dried in air.

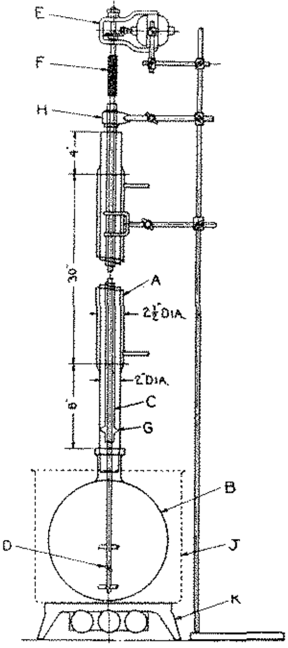


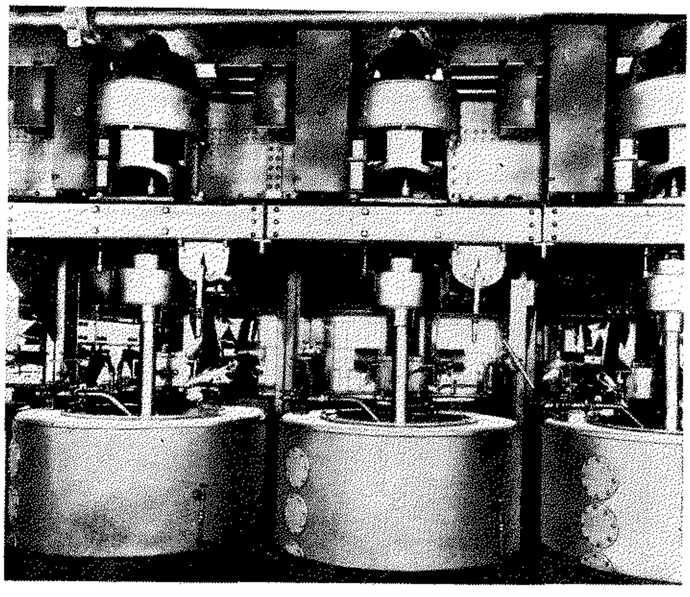
Figure 1. Apparatus for Preparation of Sucrose Octaäcetate

The yield secured in this process was 2600 to 2730 grams, or 88 to 92 per cent of theoretical.

Semi-Plant Production. The compound was also made successfully on a semi-plant scale, using a copper still of 20 gallons capacity. The amounts of reactants were proportionately the same as those used in the laboratory production. The working up of the product, however, was slightly different. After the reaction was complete and after the distillation of acetic acid had been made, the sirup was dissolved in toluene and heated to boiling with solid hydrated lime. All free acid was completely neutralized by this method before the boiling point of the solution was attained. The mixture filtered readily, and practically all the color was retained in the residue, leaving the toluene solution a very light amber color. It is possible either to use this solution directly in order to incorporate the compound into other materials of a resinous nature, or by concentration of the toluene solution to crystallize and use the acetate as a solid. Although the acetate is of crystalline form, it was found to change into a clear, transparent, colorless glass after fusion and cooling. This property alone suggests its use in plastics, resins, and like materials, together with a variety of possible combinations in various specialized commercial processes.

The melting point of the crystalline solid was found to be 68° to 69° C., although the observation varied considerably with the rate of heating, owing to the high viscosity of the compound at its melting point. Decomposition and subsequent charring occurred at about 285° C., but the compound has been distilled unchanged at 260° C. in the vacuum produced by a Cenco Hyvac oil pump. The density using the glasslike resinous form was found to be 1.28 at 20° C. Its viscosity at 100.2° C. was equal to 29.54 poises.

A sample of the product was recrystallized from alcohol five times and its optical rotation measured in chloroform. The average result was $[\alpha]_D^{24} = +59.79°$. In comparison to this result is the value $[\alpha]_D^{20} = +59.6°$, given by Hudson



Centrifugal Machines

TABLE I. SOLUBILITIES OF SUCROSE OCTAÄCETATE, OCTAPROPIONATE, AND OCTABUTYRATE AT 25° C.

SOLVENTS	SUCROSE OCTAACETATE[a]	SUCROSE OCTAPROPIONATE	SUCROSE OCTABUTYRATE
Methyl alcohol	+	+	+
Ethyl alcohol	+	+	+
Butyl alcohol	Partial	+	+
Isobutyl alcohol	—	+	+
Isopropyl alcohol	+	+	+
Isoamyl alcohol	+	+	+
Mixed amyl alcohols	Partial	+	+
Diacetone alcohol	+	+	+
Diethylene glycol	—[b]	—	+[c]
Propylene glycol	—[b]	—	+[c]
Acetone	+	+	+
Methyl acetate	+	+	+
Ethyl acetate	+	+	+
Butyl acetate	+	+	+
Amyl acetate	+	+	+
Mixed amyl acetates	+	+	+
Ethyl ether	+	+	+
Isopropyl ether	—	+	+
Dichlorethyl ether	+	+	+
Dioxan	+	+	+
Cellosolve	+	+	+
Methyl cellosolve	+	+	+
Diethyl cellosolve	+	+	+
Butyl cellosolve	+	+	+
Butyl carbitol	+	+	+
Benzene	+	+	+
Xylene	+	+	+
Toluene	+	+	+
Mixed amyl chlorides	+	+	+
Chloroform	+	+	+
Ethylene dichloride	+	+	+
Ethylene chlorhydrin	+	+	+
Chlorobenzene	+	+	+
Benzyl chloride	+	+	+
Castor oil	Ppts.	—	+
Cod liver oil	—	Partial	+
Cottonseed oil	—	Partial	+
Boiled linseed oil	—	Partial	+
Turpentine	—	+	+
Gasoline	—	Partial	+
Benzyl benzoate	+	+	+
Benzaldehyde	+	+	+

[a] + = completely soluble; — = insoluble.
[b] Swells.
[c] Emulsifies.

and Johnson (*2*). The refractive index of the fused form of the substance was $n_{\mathrm{D}}^{20} = 1.4660$.

Some electrical properties of sucrose octaäcetate are as follows:

	60 CYCLES	10^3 CYCLES	10^6 CYCLES
Dielectric const.	4.3	4.5	4.7
Power factor, %	12.3	5.8	1.7

Resistivity = 1.5 × 10^8 megohm-cm.

The amount of free acid (acetic) contained in the crystals, after washing and drying, averaged in most cases about 0.03 per cent. The stability of the compound to water, made by boiling one gram with water for one hour, showed by titration that 0.25 per cent of all available acetic acid was split off by hydrolysis. In water at 40° C. for 5 days the hydrolysis amounted to 0.20 per cent of the available acetic acid. The solubility of the compound in water was 0.14 per cent. It is intensely bitter; between 0.001 and 0.002 mg. in one cc. of water can be detected by taste. The solubility in other solvents is listed in Table I.

SUCROSE OCTAPROPIONATE AND OCTABUTYRATE

Sucrose octapropionate and the octabutyrate were prepared in a somewhat similar manner. The first, a low-melting crystalline solid, was found to form, after fusion, a semi-hard glass readily crystallizable when submerged in water, although its solubility in this solvent was less than 0.01 per cent. Its melting point was 45.4° to 45.5° C. and its viscosity measured at 48.9° C. was 47.8 poises. The density at 20° was 1.1849.

Sucrose octabutyrate, which is an uncrystallizable viscous sirup, exhibited a decidedly oily character. Its viscosity measured at 25.9° C. was 32.7 poises. The Saybolt viscosity at 210° F. (98.9° C.) was 120 seconds, and at 100° F. (37.8° C.), 2400 seconds. The density measured at 20° C. was 1.1232. Its solubility in water was similar to that of the octapropionate—i. e., less than 0.01 per cent.

The solubilities of the esters of sucrose previously mentioned, as shown in Table I, were found by observing the behavior of 0.5 gram of solute in 5 cc. of solvent.

Further investigations on the properties and applications of these compounds are being undertaken.

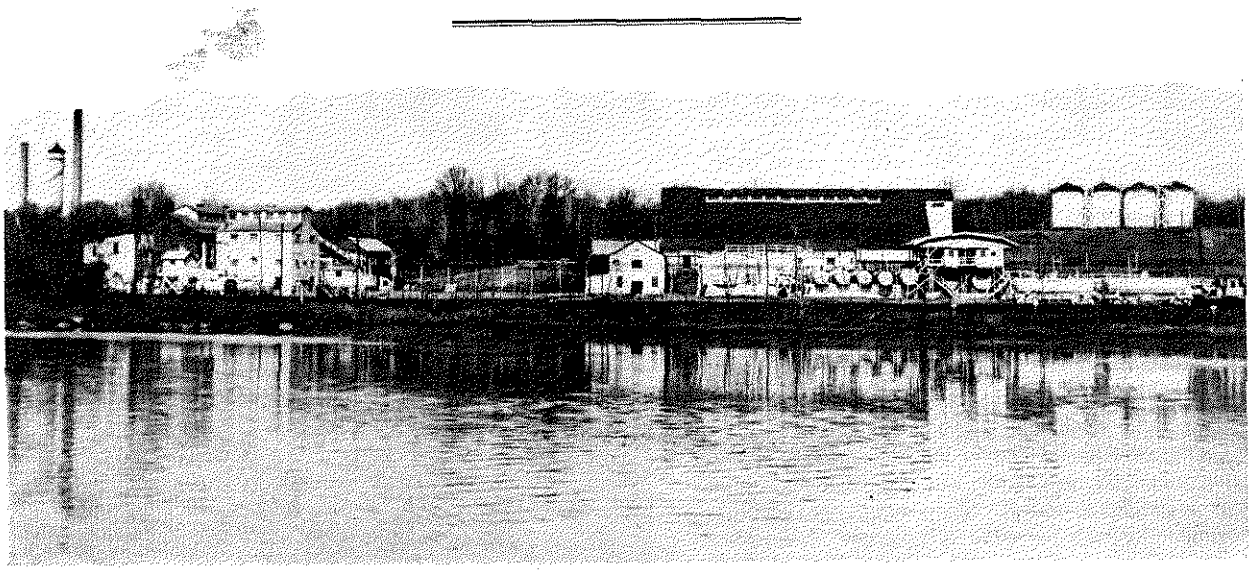
LITERATURE CITED

(1) Herzfeld, A., *Z. Ver. deut. Zucker-Ind.*, **37**, 422 (1887).

(2) Hudson, C. S., and Johnson, J. M., *J. Am. Chem. Soc.*, **37**, 2753 (1915).

(3) Schutzenberger, P., *Compt. rend.*, **61**, 485 (1865).

RECEIVED April 13, 1933.



NITRIC ACID PLANT (see page 980)