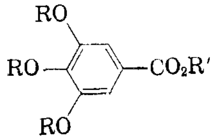
TABLE I

3,4,5-TRIALKOXYBENZOIC ACIDS AND ESTERS,



Compound		M.P. or B.P., °C.	Analyses, %			
			Carbon		Hydrogen	
R	R′		Calcd.	Found	Calcd.	Found
C_2H_5	$C_6H_{15}ClN$[a]	128–130	58.52	58.59	8.27	8.22
$C_6H_5CH_2$	$C_6H_{15}ClN$[a]	153–155	70.87	70.51	6.65	6.92
n-C_3H_7	H	89–91	64.84	65.06	8.16	8.12
n-C_3H_7	$C_6H_{15}ClN$[a]	125–126	61.16	60.82	8.87	8.98
n-C_4H_9	H	68.5–70	67.43	67.45	8.94	9.01
n-C_4H_9	CH_3	190–195/1 mm.	68.15	68.37	9.15	9.42
n-C_5H_{11}	CH_3	203–205/1 mm.	70.01	69.71	9.71	9.58

[a] $C_6H_{15}ClN = CH_2CH_2N(C_2H_5)_2 \cdot HCl$.

mole) of the ester and 0.9 mole of sodium ethoxide, in 1 l. of absolute ethanol was stirred and heated to reflux. A solution of 181.2 g. (1.2 moles) of n-amyl bromide in 100 ml. of alcohol was added dropwise, and the reaction mixture was heated for 10 hr. It was worked up in a fashion similar to that described in the preceding experiment. Distillation of the residue which remained after concentration of the ether solution yielded 48.5 g. (41%) of the ester; b.p. 203–205°/1 mm., n_D^{20} 1.4971.

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Isolation of Maltose from Honeydew on Alsike (*Trifolium hybridum*) Seeds[1]

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Recently Northrup King and Company, Minneapolis, drew our attention to the presence of a sticky substance on alsike (*Trifolium hybridum*) seeds harvested in Idaho. The material, a type of honey dew arising from infestation of the plants by aphids, *Therioathis maculata* (Buckton), was obtained by washing the seeds with water, filtering, and concentrating the brownish yellow filtrate *in vacuo* to a sirup. This sirup reduced Fehling solution and gave a positive Molisch test. Paper chromatographic analysis, using three different solvents; 1-butanol:ethanol:water, (4:1:5);[2] 1-propanol:water azeotrope;[3] ethylacetate : pyridine:water (2.5:1.0:3.5)[4] and p-anisidine phosphate spray,[5] revealed the presence of glucose, fructose, maltose, maltotriose, and other more slowly moving components.[6] Inasmuch as the material arose from aphids it was expected that one of the components might be melezitose[7] but none was present. The maltose component was separated by sheet paper chromatography using Whatman No. 3 paper and the above pyridine-ethyl acetate-water solvent in the usual way and extracted from the appropriate segments of the paper with water. Removal of the solvent *in vacuo* produced a colorless sirup which crystallized when dissolved in the minimum quantity of water and treated with ethanol to incipient turbidity. The crystalline product proved to be maltose, melting point and mixed melting point 118–123°, $[\alpha]_D^{22}$ + 126° in water (c, 0.5). The maltose was further characterized by reduction with sodium borohydride[8] to maltitol which was tranformed by means of sodium acetate and acetic anhydride into the crystalline nonacetate,[9,10] melting point and mixed melting point 82–83°.

Paper chromatography has shown in other experiments that the honey dew exuded by the leaves of a young peach tree (*Amygdalus sp.*) contained glucose, fructose, and sucrose; that from the leaves of a House Balsam (*Impatiens sultani*) contained

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[1] Paper No. 3789 of the Scientific Journal Series, Minnesota Agricultural Experiment Station.

[2] S. M. Partridge, *Nature*, **158**, 270 (1946).

[3] F. Smith and H. C. Srivastava, *J. Am. Chem. Soc.*, **78**, 1404 (1956).

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[6] C. J. P. Wolf and W. H. Ewart, *Arch. Biochem. and Biophys.*, **58**, 365 (1955); R. H. Hackman and Trikojus, *Biochem. J.*, **51**, 653 (1952).

[7] C. S. Hudson and S. F. Sherwood, *J. Am. Chem. Soc.*, **42**, 116 (1920).

[8] M. Abdel-Akher, J. K. Hamilton, and F. Smith. *J. Am. Chem. Soc.*, **73**, 4691 (1951).

[9] M. L. Wolfrom and T. S. Gardner, *J. Am. Chem. Soc.*, **62**, 2553 (1940).

[10] P. Karrer and J. Büchi, *Helv. Chim. Acta*, **20**, 86 (1937).

only sucrose which crystallizes on the plants while the nectar from flowers of the Poinsettia (*Poinsettia sp.*) contained glucose, fructose, and sucrose.

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Cation Exchange Resins as Catalysts in the Alkylation of Phenols

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Both anion and cation exchange resins have been widely used as catalysts for reactions such as esterification, hydrolysis, and sucrose inversion[1,2]—reactions which involve only carbon-oxygen bonds. By comparison, reports of the use of resins (particularly cation exchange resins) as catalysts for reactions in which carbon–carbon bonds are formed, are few. Ion exchange resins are reported to catalyze cyanohydrin formation, aldol condensation,[3,4] and the various modifications of the Knoevenagel[5] and Michael[6] condensations. It seemed of interest to investigate other reactions which are normally catalyzed by strong acids, to see whether cation exchange resins could be used in place of the usual Lewis acids.

It has been found that the sulfonic acid type cation exchange resins are excellent catalysts for the alkylation of phenol with olefins such as isobutylene, diisobutylene, and nonene-1.

The resins investigated were Amberlite IR-112 and IR-120, Dowex 50 × 12, and Permutite Q; all were sulfonic acid type resins. The conversion[7] was a little lower when Amberlite IR-112 was used, but all other results were independent of the resin used.

The yields in these alkylations were essentially independent of the concentration of resin.

When phenol was alkylated with isobutylene using a cation resin there was generally no *ortho* isomer in the product.

The presence of water was deleterious, at least in the diisobutylene alkylation reactions, for when the resin was used after only air drying, no reaction occurred. The reaction required an oven-dried resin. Drying of the diisobutylene also increased the yield.

The use of a cation exchange resin as catalyst has the particular advantage over a mineral acid catalyst that at the conclusion of the reaction, a simple filtration of the molten reaction mixture leaves an acid-free solution ready for distillation. There is no chance of acid catalyzed rearrangement during the distillation, and the product is a high purity *p*-alkylphenol. In addition, the use of resins as catalysts eliminates by-products formed by reaction of the mineral acids with the phenol, and by by-products due to polymerization or degradation of the olefin.

Attempts to alkylate xylene and benzene using a resin catalyst were unsuccessful.

EXPERIMENTAL

Preparation of resin catalyst. The resins which are normally purchased in the salt form were converted to the acid form by washing with 5% H_2SO_4 until the wash water gave a negative flame test for sodium. The resin was then thoroughly washed with distilled water until the wash water was neutral, air dried for 24 hr., and then heated for 18 hr. in a vacuum oven at 100–120°.

The resin may be washed with acetone and ether, following the air drying, to remove traces of colored organic impurities. This treatment has no effect on the catalytic activity of the resin.

The resins were all commercial materials: Amberlite IR-112 and IR-120, 16 to 50 mesh (Rohm & Haas), Permutite Q, approx. 20 to 60 mesh (Permutite Corp.), and Dowex 50 × 12, 200–400 mesh (Dow Chemical).

p-tert-Octylphenol[8] (*p-diisobutylphenol or 1,1,3,3-tetramethylbutylphenol*). A typical preparation is given. Phenol (250 g., 2.6 moles), diisobutylene, (328 g., 219 moles), and 17.5 g. of Amberlite IR-112, prepared as described above, were heated together with vigorous stirring for 24 hr. at 70–75°.

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(1) (a) S. Sussman in *Ion Exchange—Theory and Application*, F. C. Nachod, ed., Academic Press Inc., New York, N. Y., 1949, p. 265. (b) F. C. Nachod, *Ion Exchange Catalysis*, L. Farkas Memorial Volume, A. Farkas, E. P. Wigner, eds., Research Council of Israel, Jerusalem, 1952, p. 188.

(2) (a) R. Kunin and R. J. Meyers, *Ion Exchange Resins*, John Wiley and Sons, New York, N. Y., p. 137, 1950. (b) F. X. McGarvey and R. Kunin in *Ion Exchange Technology*, F. C. Nachod and J. Schubert, eds., Academic Press Inc., New York, N. Y., 1949, p. 265.

(3) C. J. Schmidle and R. C. Mansfield, *Ind. Eng. Chem.*, **44**, 1388 (1952).

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(6) E. D. Bergmann and R. Corett, *J. Org. Chem.*, **21**, 107 (1956).

(7) For greater ease in discussing the results of these experiments, the terms "conversion" and "yield" are employed. Percent conversion represents the percent of theoretical value based on the amount of (limiting) starting material charged to the reaction. Percent yield represents the percent of the theoretical value based on the amount of starting material used up (or not recovered) during the reaction.

(8) As used here, *p-tert*-octylphenol refers to the alkyl group 1,1,3,3-tetramethylbutyl-, which results from the alkylation of phenols with diisobutylene (DIB). DIB is a mixture of two isomers, 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene which are assumed to give identical alkylation products.