lowed by addition of dry ether. A yield of 12.3 g. (47%) of slightly yellow crystals, m. p. 316–317°, was obtained.

Anal. Calcd. for $C_{21}H_{22}ON_2.2HBr$ (480.23): C, 52.52; H, 5.04; equiv. wt., 240.1. Found: C, 52.47; H, 5.01; equiv. wt., 240.0, 240.8 ($AgNO_3$ titration).

2 - Quinolyl - 2 - piperidylmethane.[23,24]—A solution of 3.0 g. of *o*-aminobenzaldehyde,[25] 3.0 g. of 2-piperidylacetone,[26] 10 ml. of methanol, 40 ml. of water and 2 ml. of 6 *N* sodium hydroxide was warmed on the water-bath for two hours. Excess methanol was allowed to evaporate and the mixture acidified with hydrochloric acid and extracted with chloroform to remove colored impurities. The solution was made alkaline and extracted twice with chloroform and the dried combined extracts were distilled to give the following fractions: 1.0 g. of 2-piperidylacetone, b. p. 60–90° (2 mm.); 2.6 g. yellow oil, b. p. 160–165° (2 mm.). The yellow oil was converted to the hydrochloride and recrystallized twice from a mixture of 10% methanol in absolute ethanol to give colorless needles, m. p. 218–219°.

The same hydrochloride, as shown by lack of depression of the melting point upon mixture of the two products, was prepared similarly by condensation of N-acetyl-2-piperidylacetone, b. p. 200–208° (1.0 mm.), and subsequent hydrolysis by two hours of boiling in 6 *N* hydrochloric acid.

Anal. Calcd. for $C_{15}H_{18}N_2 \cdot HCl$: C, 68.57; H, 7.29; equiv. wt., 262.7. Found: C, 68.59; H, 7.35; equiv. wt., 260.0 ($AgNO_3$ titration).

Summary

The syntheses have been reported of α-(2-piperidyl)-quinolinemethanols having the 2-piperidylcarbinol group attached to the 2-, 3-, 5-, 6- and 7-positions in the quinoline nucleus; also of 2-phenyl-α-(2-piperidyl)-5-quinolinemethanol and 8-chloro-α-(2-piperidyl)-5-quinolinemethanol. Various quinoline carboxylic ester intermediates and related substances have been described.

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[23] The structure of this compound was not definitely ascertained. Numerous attempts to oxidize the methylene group were unsuccessful; butyl nitrite, chromic acid and lead tetraacetate were tried and failed to give isolable products.

[24] Condensation of 2-picolyllithium with 2-chloroquinoline failed to give appreciable yields of 2-quinolyl-2′-pyridylmethane in preliminary experiments.

[25] Bamberger and Demuth, *Ber.*, **34**, 1329 (1901). The yield of pure *o*-aminobenzaldehyde, b. p. 80–85° (2 mm.), was 55–67%.

[26] Hess and Eichel, *ibid.*, **50**, 1404 (1917).

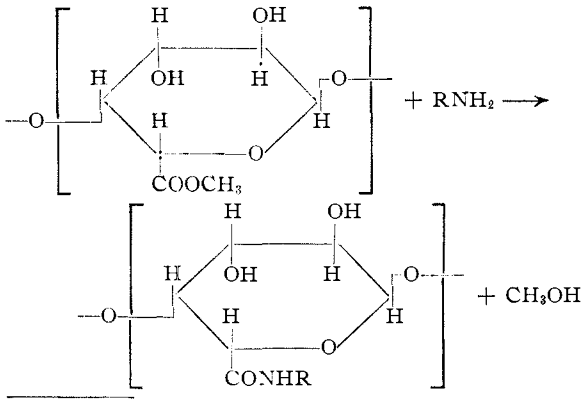
NOTES

Some Polygalacturonide *n*-Alkylamides

BY J. F. CARSON

This paper describes the preparation and properties of several polygalacturonide *n*-alkylamides. Although the neutralization of pectic acids with various amines to yield amine salts has been described,[1] the conversion of the carbomethoxyl groups of pectins to amide groups has not been recorded in the literature.

The amides were prepared by reaction of dry pectins with primary aliphatic amines under anhydrous conditions according to the scheme



Two sets of pectic material were used—one a commercial citrus pectin in which approximately three-fourths of the carboxyl groups were esterified as methyl ester, and the other a polygalacturonide methyl ester with a free acid content of approximately 3%, calculated as anhydrogalacturonic acid. By this reaction, the *n*-propyl- and *n*-butylamides of pectin were prepared, and the ethyl-, *n*-propyl-, *n*-butyl-, *n*-hexyl- and *n*-octylamides were prepared from polygalacturonide methyl ester. Nitrogen and methoxyl analyses indicated that the reaction with ethyl-, *n*-propyl- and *n*-butylamine was substantially complete after seventy-two hours at room temperature; with *n*-hexylamine, reaction was approximately 95% complete, and with *n*-octylamine only 50%. Repeated treatment of the partially reacted octylamide with excess octylamine at 50° increased the extent of the reaction, but did not bring about complete replacement of the ester groups.

The ethyl-, *n*-propyl- and *n*-butylamides were soluble in water to give solutions of low viscosity. They were also soluble in formamide, swelled in the lower alcohols and aliphatic amines, and were generally insoluble in organic solvents. Recovery of the amides from aqueous solution by precipitation into large volumes of ethanol or acetone was difficult, because of the tendency of the products to separate as fine flocs. Aqueous solutions of the ethyl-, propyl- and butylamides prepared from

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[1] R. F. Stuewer and A. G. Olsen, *J. Am. Ph. Assn.*, **29**, 303 (1940).

polygalacturonide methyl ester could tolerate the addition of ethanol in concentrations as high as 50% without precipitation. Propyl- and butylamides prepared from pectin or polygalacturonide methyl ester produced very stable foams in aqueous solution. Qualitatively the amides prepared from the polygalacturonide methyl ester were more effective in this respect than the corresponding amides prepared from commercial pectin, and the *n*-propylamides[2] produced more stable foams than the *n*-butylamides. The reaction of pectin with amines apparently proceeds with degradation of the polygalacturonide chain, since the conversion of pectin to its *n*-butylamide was accompanied by a decrease in intrinsic viscosity[3] from 3.8 to 1.0. The amides had no jelly-forming properties. The hexyl- and octylamides were insoluble in water and organic solvents, and swelled in formamide.

The amides prepared from pectin could be precipitated from their aqueous solutions by small quantities of copper, nickel or lead ions, but not by calcium even in concentrations as high as 5%. The amides prepared from polygalacturonide methyl ester, with a low free acid content, were not precipitated by these ions. Propyl- or butylamides in 0.5% aqueous solution did not precipitate in the presence of 5% copper sulfate or lead nitrate. This fact is good evidence in the latter case for the presence of a true amide linkage rather than salt formation, since the polygalacturonide ion could be precipitated from amine salts by copper or lead.

As supporting evidence for the structures assigned, the specific conductances in 0.1% aqueous solution of the polygalacturonide *n*-propylamide, polygalacturonide methyl ester and the propylamine salt of polygalacturonic acid (prepared by enzymic hydrolysis of the polygalacturonide methyl ester) were found to be, respectively, 6.813×10^{-5}, 7.594×10^{-5} and 21.61×10^{-5} ohms^{-1} cm.$^{-1}$. The relatively close agreement between the conductances of the methyl ester and of the amine reaction product indicates that salt formation was not significant. The amides on hydrolysis with acid or alkali yielded the corresponding amines and pectic acid identified by uronic anhydride analyses and enzymatic hydrolysis to galacturonic acid. The amides and their analyses are recorded in Table I.

TABLE I

POLYGALACTURONIDE *n*-ALKYLAMIDES

Starting material	Amide	Nitrogen analyses, % Calcd.[a]	Nitrogen analyses, % Found	Residual methoxy,[b] %
Pectin	*n*-Propyl	4.42	4.50	0.3
	n-Butyl	4.23	4.24	.5
Polygalacturonide methyl ester	Ethyl	6.17	6.05	.7
	n-Propyl	5.81	5.98	.5
	n-Butyl	5.49	5.85	.5
	n-Hexyl	4.94	4.75	1.6
	n-Octyl	4.50	2.74	6.4

[a] Theoretical nitrogen contents were calculated assuming complete reaction of the methyl ester groups and no loss of non-uronide material. [b] Methoxyl analyses were performed by the Vieböck–Schwappach modification of the Zeisel method, E. P. Clark, *J. Assoc. Official Agr. Chem.*, **15**, 136 (1932). All samples were humidified over water and re-dried for analysis. Methoxyl determinations were performed by Miss Nylan Jeung.

Experimental

Pectin.—The pectin was a commercial citrus pectin and was de-ashed by passage through ion exchangers. It had the analysis: ash, 0.18; methoxyl, 10.7 (Zeisel or saponification method); uronic anhydride, 81.6.

Polygalacturonide Methyl Ester.—This material was prepared by a modification of the procedure of Morell, Baur and Link.[4] The method varied, in that pectin rather than pectic acid was used as a starting material, and milder conditions of esterification were employed. Anhydrous citrus pectin, 120 g., and 600 ml. of 1% methanolic hydrochloric acid were stirred together under anhydrous conditions for thirty-eight hours at 60-62°. The product was recovered by filtration and was washed with absolute methanol until free of chlorides, and then with ether. A yield of 107 g. of polygalacturonide methyl ester was obtained having the analysis: methoxyl, 14.5 (Zeisel or saponification); uronic anhydride, 84.7; free acid, 3.0 (direct titration).

Polygalacturonide *n*-Propylamide.—The preparation of this amide is typical and the procedure is described in detail. A mixture of 11 g. of dry polygalacturonide methyl ester and 30 g. of anhydrous *n*-propylamine in a glass-stoppered flask was shaken mechanically for four hours. The polygalacturonide methyl ester dissolved in the amine and later the reaction solution coagulated as a solid gel. The gel structure was broken up with a spatula, an additional 20 g. of amine was added, and the reaction mixture was allowed to stand for three days. The gelatinous amide was converted to a granular material by trituration with 200 ml. of ether. The ether was removed by centrifugation and the amide washed successively with 2% ethanolic hydrochloric acid to remove excess amine, neutral 95% ethanol, and ether. A yield of 12.4 g. (quantitative) of polygalacturonide *n*-propylamide was obtained as a white odorless powder. The preparation of amides from commercial pectin followed essentially the same procedure except that the pectin did not dissolve in the amine, but gradually swelled and lost its grainy structure. Both the polygalacturonide methyl ester and the pectin were used in the form of a fine powder, and were dried *in vacuo* (5 mm.) at 70° over phosphorus pentoxide.

Hydrolysis of Polygalacturonide *n*-Butylamide.—A solution of 10 g. of amide, prepared from pectin, in 500 ml. of 3% hydrochloric acid was kept at 40° for two weeks, the solution setting to a solid gel on the second day. Eight grams of pectic acid was isolated having the analyses: ash, 3.0; methoxyl, 0.2; uronic anhydride, 86; nitrogen, 0.08.

A sample of the pectic acid on treatment with a commercial pectic enzyme, according to the procedure of Frush and Isbell,[5] yielded galacturonic acid (75%) isolated as the sodium strontium salt.

Alkaline hydrolysis of polygalacturonide *n*-butylamide by 0.2 *N* potassium hydroxide for eighteen hours at 23° likewise yielded butylamine and pectic acid.

WESTERN REGIONAL RESEARCH LABORATORY
BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY
AGRICULTURAL RESEARCH ADMINISTRATION
U. S. DEPARTMENT OF AGRICULTURE
ALBANY, CALIFORNIA

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[2] Stuewer and Olsen (ref. 1) observed that the propylamine salt of pectic acid had foam-producing properties.

[3] Intrinsic viscosities were determined in 0.9% aqueous sodium chloride solution at *p*H 7.

[4] S. Morell, L. Baur and K. P. Link, *J. Biol. Chem.*, **105**, 1 (1934).

[5] H. L. Frush and H. S. Isbell, *J. Research Natl. Bur. Standards*, **33**, 401 (1944).