described by Ritter and Fleck;[7] lignin by the 72% sulfuric acid method by Ritter, Seborg, and Mitchell;[8] and the hydrolysis number by a procedure developed by Hawley and Fleck.[9] The cellulose stable to the 15% acid hydrolysis is the residue remaining from the "hydrolysis number" determination.

The results of the analysis are recorded in Table I.

TABLE I

COMPOSITION OF COCONUT SHELLS

Materials determined	Based on weight of oven-dry (105°) shells, %
Moisture	6.07
Cold H_2O soluble	1.43
Hot H_2O soluble	2.67
Ether soluble	0.19
1% alkali soluble	20.53
Lignin	33.30
Total pentosan	30.28
Ash	0.23
Holocellulose	61.00
Cellulose	44.98
Pentosans in cellulose	17.67
Pentosan in cellulose	39.30[a]
Loss in cellulose due to 15% H_2SO_4 hydrolysis, "Hydrolysis No."	35.85[a]
Cellulose stable to 15% H_2SO_4 hydrolysis	28.86
Methoxyl	5.39
Acetic acid by hydrolysis	4.79
Loss in weight of shells due to 2.5% H_2SO_4 hydrolysis from acetic acid determination	18.74

[a] On basis of Cross and Bevan cellulose.

(7) Geo. J. Ritter and L. C. Fleck, *Ind. Eng. Chem.*, **16**, 147 (1924).

(8) J. Ritter, R. M. Seborg, and R. L. Mitchell, *Ind. Eng. Chem., Anal. Ed.*, **4**, 202 (1932).

(9) L. F. Hawley and L. C. Fleck, *Ind. Eng. Chem.*, **19**, 850 (1927).

Discussion of Results

The results indicate that the coconut shells have higher percentages of lignin, total pentosans, and pentosans in the cellulose than do the hardwoods. On the other hand, the percentages of the cellulose, the cellulose stable to a 15% sulfuric acid hydrolysis, and the holocellulose, which is the total carbohydrate material in the extractive-free shells, are considerably lower than the values of the corresponding materials in hardwoods. The acetic acid content and the methoxyl content of the shells are about the same as those of hardwoods.

Summary

Coconut shells have been analyzed by methods that have been developed for woods. The yields of lignin and pentosans from the shells are higher than those from woods. Conversely, the yields of holocellulose and Cross-Bevan cellulose from the shells are considerably lower than those from woods. The methoxyl content and the acetic acid content are about the same in the two materials.

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Preparation of Para-Aminobenzoic Acid Esters of Monoalkylamino Alcohols

BY SAMUEL D. GOLDBERG AND WILLET F. WHITMORE

Dialkylamino alcohols in the form of their esters with *p*-aminobenzoic acid have been used as local anesthetics for a long time. However, an examination of the literature reveals that no work has been reported on the preparation of analogous compounds where the monoalkylamino alcohols have been employed. The present investigation deals with the preparation of compounds of the latter type.

It was hoped to increase the anesthetic efficiency of the compounds without unduly increasing their toxicity in proportion to their increased molecular weight, since monosubstituted amino alcohols were used. For example, the monobutylamino alcohol ester has the same molecular weight as the diethylamino alcohol ester used in procaine. It was hoped also that these compounds would show some vaso-constrictor properties, in contrast to the dialkylamino compounds, since most of the vaso-constrictors have monoalkyl substituted amino nitrogen in their configuration.

Some monoalkylaminoethanols have been prepared by Knorr,[1,2] Mathes,[3] J. S. Pierce[4] and two members of the monoalkylaminopropanol series by Pierce and Adams.[5]

(1) Knorr, *Ber.*, **22**, 2088 (1899).

(2) Knorr and Schmidt, *ibid.*, **31**, 1072 (1898).

(3) Mathes, *Ann.*, **315**, 104 (1901).

(4) Pierce, THIS JOURNAL, **50** 241 (1928).

(5) Pierce and Adams, *ibid.*, **45**, 790 (1923).

The literature indicates that all of the common alkyl groups have been used in the preparation of the monoalkylated aminoethanols with the exception of the *n*-amyl compound, which is here reported on. In the monoalkylaminopropanol series, the only two described in the literature were the methyl and *n*-amyl compounds. In this investigation the monoethyl-, *n*-propyl- and *n*-butylaminopropanols were prepared and are described.

The original methods of preparation of the ethanol series consisted in the addition of ethylene oxide or ethylene chlorohydrin to an aqueous solution of a primary amine. Because of the difficulty in isolation and purification of the desired product from the various by-products which are formed, these procedures were considered impracticable. The following method which finally was adopted was one that worked smoothly and obviated the previous difficulties.

Aniline is monoalkylated by the well-known methods, and then treated in the cold with ethylene oxide, in a pressure flask or a similar tightly stoppered vessel. After standing for several days, the monoalkylated aniline is converted to the hydroxyethylalkylaniline in practically a theoretical yield. This latter compound is then converted into the *p*-nitroso derivative by treatment with hydrochloric acid and sodium nitrite, and then this material is refluxed with concentrated sodium hydroxide. The last step results in the hydrolysis of the *p*-nitroso substituted amine, and when the reaction mass is steam distilled the secondary amino alcohol (ethanol series) comes over and is recovered from the distillate.

The yield of pure monoalkylaminoethanol averages about 35% of theoretical.

The preparation of the monoalkylaminopropanols was effected by the action of trimethylene oxide and trimethylene bromohydrin on the primary amine.

The preparation of the *p*-aminobenzoic esters of the amino alcohols was effected by the condensation of the amino alcohols with *p*-nitrobenzoyl chloride in an aqueous alkaline solution. Temperature control was found to be important and the reaction gives optimum yields at 30° to 40°. The esters prepared were oils in all cases, excepting that of the *n*-amyl ester of the ethanol series, which was a yellow solid.

The reduction of the nitro compounds was effected by means of tin and hydrochloric acid. In all cases well-defined crystalline hydrochlorides were produced.

Experimental Part

Butylhydroxyethylaniline, $C_4H_9N(CH_2CH_2OH)C_6H_5$.—One mole of *n*-butylaniline was placed in a pressure bottle and ethylene oxide (0.95 mole) was added at room temperature. This is possible because the sudden expansion when ethylene oxide is liberated from a cylinder permits the gas to chill the container below the boiling point of the ethylene oxide. The oxide forms a double layer with the alkylaniline compound and on mixing goes into complete solution. The bottle was then allowed to stand about three weeks at room temperature, when a thick viscous oil was obtained. Upon fractional distillation, the theoretical yield of the butylhydroxyethylaniline was obtained; b. p. 300° at 760 mm. There were no by-products.

The tertiary amine obtained above was then converted into its *p*-nitroso derivative by treating with hydrochloric acid and sodium nitrite, as follows: to one mole of butylhydroxyethylaniline was added two moles of hydrochloric acid and the mixture was cooled to 5°. Sodium nitrite was then added in excess and when the formation of the nitroso compound was completed the whole was transferred to a dropping funnel, and allowed to drop upon a hot 50% solution of sodium hydroxide and finally steam distilled. The distillate was then extracted with ether, the solvent evaporated, and the residual oil fractionated. The pure *n*-butylaminoethanol had a boiling point of 198–200° at 760 mm.; yield 33%.

The isobutyl- and *n*-amylethanols were made the same way, with corresponding yields. The amyl compound $C_5H_{11}NHC_2H_4OH$ was also made by the action of *n*-amylamine on ethylene oxide. The *n*-amylamine used was made by the modified Curtis reaction,[6] employing caproyl chloride and sodium azide.

The preparation of picrates of these amino alcohols by the conventional method employing the use of absolute alcohol as a solvent, was very tedious and gave poor results. The picrates of all the secondary aminoethanols and secondary aminopropanol compounds were prepared in the following manner: 0.01 mole of picric acid was dissolved in 10–15 cc. of boiling xylene, to which was added 0.01 mole of the amino alcohol. The immediate precipitation of a dark oily picrate resulted. The supernatant liquid was decanted and the oil again treated with xylene. This was repeated a second time and the residual oil was then extracted with benzene, which, upon cooling, yielded a pure yellow crystalline picrate.

The Preparation of *n*-Butylaminopropanol, ($C_4H_9NHC_3H_6OH$).—Fifteen hundredths mole of *n*-butylamine and 0.15 mole of trimethylene oxide (made by the action of trimethylene bromohydrin on 50% sodium hydroxide) were placed in 75 cc. of water and allowed to stand for twenty hours. The mixture was then treated with solid sodium hydroxide, extracted with ether, dried, and distilled. The resultant products were oily liquids with a slight ammoniacal odor.

We are presenting a complete table (Table I) of both series of amino alcohols, those presented here for the first

(6) C. Naegeli and E. Vogt-Marcus, *Helv. Chim. Acta*, **15**, 60–74 (1932).

TABLE I

Ethanol derivative	Formula	B. p., °C.	Mol. wt.	Ref. index	Sp. gr.	Analyses of picrates, % N Calcd.	Found	M. p. of picrates, °C.
Monomethyl		159	75	1.4385	0.9370			
Ethyl		167.9	89	1.4440	.9140			
n-Propyl		181	103	1.4428	.9005			
Isobutyl		186	117	1.4402	.8818			
n-Butyl		199–200	117	1.4437	.8907			
n-Amyl	$C_7H_{17}ON$	214–216	131	1.4508	.8814	15.50	15.81	57–58
n-Hexyl		231	145	1.4472	.8829			
Propanol der.								
Methyl		167–169	89	1.4418	0.9315			
Ethyl	$C_6H_{13}ON$	181	103	1.4550	.9140	16.90	17.07	92–93
n-Propyl	$C_6H_{15}ON$	199–200	117	1.4519	.9012	16.16	16.30	86–87
n-Butyl	$C_7H_{17}ON$	213–215	131	1.4529	.8902	15.30	15.53	66–67
n-Amyl	$C_8H_{19}ON$	233	145	1.4534	.8830	14.92	14.70	61–63

TABLE II

Ethanol series	M. p. of HCl, °C.	M. p. base, °C.	Formula	Analyses of hydrochloride, % C, calcd.	C, found	H, calcd.	H, found	N, calcd.	N, found
n-Propyl	160	..	$C_{12}H_{19}N_2O_2Cl$	56.70	56.92	7.36	7.60	10.85	11.03
n-Butyl	146	75	$C_{13}H_{20}N_2O_2Cl$	57.30	56.95	7.34	7.70	10.30	10.54
Isobutyl	192–194	..	$C_{13}H_{20}N_2O_2Cl$	57.30	56.91	7.34	7.70	10.30	10.22
n-Amyl	152–153	66	$C_{14}H_{22}N_2O_2Cl$	58.50	58.69	7.68	8.00	9.80	9.58
Isoamyl	148–150	..	$C_{14}H_{22}N_2O_2Cl$	58.50	57.72	7.68	7.92	9.80	9.70
Propanol series									
n-Propyl	201–202	70	$C_{13}H_{20}N_2O_2Cl$	57.30	57.02	7.34	7.42	10.30	10.22
n-Butyl	196–197	56	$C_{14}H_{22}N_2O_2Cl$	58.50	58.53	7.68	8.00	9.77	9.50
n-Amyl	149–150	76	$C_{15}H_{24}N_2O_2Cl$	59.60	59.50	7.98	8.35	9.38	9.35

time, and those previously described. Those for which the analyses of the picrates are given are described here for the first time. We wish to call attention to the similarity in boiling points between the alcohols of the two series having the same molecular weight.

The preparation of monobutylaminoethyl *p*-aminobenzoate, $C_4H_9NHC_2H_4COOC_6H_4NH_2$, was accomplished in the following manner: 0.1 mole of *n*-butylaminoethanol was placed in 75 cc. of water, to which was added 5 g. of solid sodium hydroxide. When solution was completed, the temperature was adjusted at 35–40° and the solid *p*-nitrobenzoyl chloride added. The reaction was controlled so that a temperature no greater than 40° was reached. An oil was soon formed. After a half hour, or when all the solid *p*-nitrobenzoyl chloride had gone into solution, the oil was separated by decantation and washed until free from sodium hydroxide; yield was 90% of theoretical. No physical constants were obtained for any of the compounds but the amyl. The oil was then reduced directly with tin and hydrochloric acid in the usual manner.

All the propanol and ethanol esters obtained were made in a similar manner. A table of constants of all the ester hydrochlorides is shown, Table II.

Pharmacology.—All the monoalkylaminoethanol esters tested proved to be good anesthetics with comparatively little toxicity. The monoalkylaminopropanol esters were very toxic and were poor anesthetics. The isobutylaminoethyl *p*-aminobenzoate showed synergism with epinephrin, and appears to have pressor action. The amyl has less pressor action. In 1% concentration the isobutyl compound can be used without epinephrin. The mono-*n*-amylaminoethyl *p*-aminobenzoate is a surface anesthetic with interesting possibilities.

Summary

1. A new series of monoalkylaminopropanols has been prepared.

2. From these alcohols, and the monoalkylaminoethanols, by combination with *p*-nitrobenzoyl chloride and reduction, a new series of esters has been prepared.

3. These esters have pronounced anesthetic properties.

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