PROJECT REPORT FORM

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Formation of Higher-Carbon Saccharinic Acids from Xylose

In previous reports the well-known formation of saccharinic acids, containing the same number of carbon atoms or less than the original sugar, has been shown, with the aid of paper chromatography of the anilide derivatives. In this report is shown the action of hot 8 N NaOH on D-xylose to give small yields of saccharinic acids, containing six carbons or more. This is the first time the formation of such "higher" saccharinic acids has been reported.

This formation of higher acids was found during a preparation of C_5 saccharinic anilides as reference compounds for the analysis of kraft black liquors. The C_5 anilides are formed in good yield, as would be expected, but the emphasis of this report is on the higher acids. The formation of such compounds may be of importance in the degradation of polysaccharides to saccharinic acids.

When hexoses or pentoses are treated with hot concentrated alkali, by the method of Nef (1), the main products are saccharinic acids either with the same number of carbon atoms (6 and 5 resp.) or with fewer carbon atoms. (See Project Report 4, pp. 2-5). There has been no evidence to date in the literature of the recombination of fragments to saccharinic acids containing more carbon atoms than the original sugar. However, workers in this field have suspected that the rearrangement of hexoses to either isomeric hexoses or C_6-saccharinic acids may

go thru a recombination of smaller fragments.

Thus Sowden and Kuenne (2) treated mannose (I), labeled with C^{14} on carbon 1, with alkali and isolated the branched-chain alpha-glucosaccharinic acid (III) as the product (see Figure 1). If rearrangement goes thru an intermediate osone (II), the side group methyl in III should be derived from carbon 1 in II and I, and hence only the carbon in this group should be radioactive. Actually only part of the radioactivity in III was in this group. The rest was in carbon 2 in the chain (equivalent to carbon 3 in II and I). So a rearrangement with recombination of smaller units must have occurred.

Recombination of smaller units is also suggested by the work of Wolfrom and Schumacher (3), and of Sowden and Blair (4). The former authors studied the effect of dilute KOH (pH 8) on fructose (IV) at 100°; the latter authors studied the effect of a strongly basic resin on glucose (V) at 40-60°. In both cases D-sorbose and L-sorbose were isolated as products. (See figure 2). The formation of D-sorbose would imply rearrangement of the asymmetric centers of either IV or V as far as carbon-$_4$, thru a 3,4-enediol, and the formation of L-sorbose would imply a rearrangement as far as carbon-5, thru a 4,5-enediol. The possibility of such enediols being formed is considered as far less satisfactory than the recombination of smaller fragments.

Sowden and Kuenne (2) have pointed out that present reaction mechanisms take into account the fact that no saccharinic acids of molecular weight higher than the original sugar have been reported. In

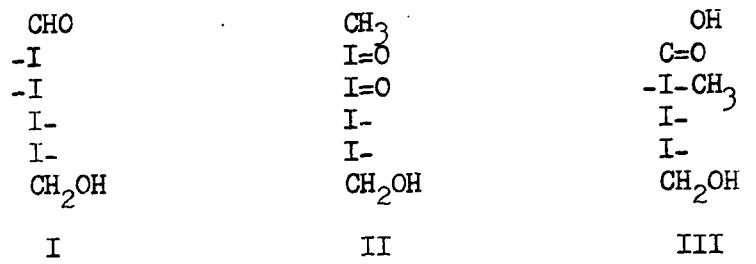

Figure 1

Rearrangement of Mannose to Alpha-Glucosaccharinic Acid

(Hyphens denote configuration of OH groups)

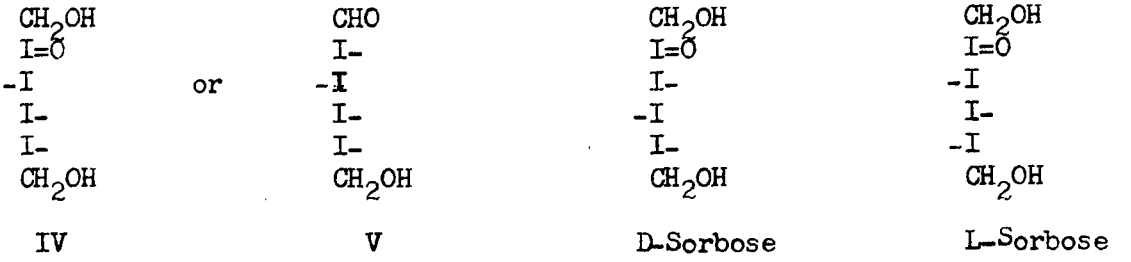

Figure 2

Formation of Sorboses from Fructose or Glucose

(Hyphens denote configuration of OH groups)

the present work chromatography of the saccharinic anilides formed from 20 grams of D-xylose has led to the isolation of 400 milligrams of material believed to be anilides of C_6-saccharinic acids and higher. These fractions move as slowly or more slowly than the C_6 metasaccharinic anilides derived from glucose, whereas the normal C_5 anilides move more rapidly.

In previous work (Report No. 3) it has been shown on paper chromatograms that the anilides of the C_3 to C_6 saccharinic acids move inversely as their molecular weights. Thus the suspected presence of the anilides of any higher saccharinic acids, derived from the C_5 sugar xylose, should be shown by spots on the paper chromatogram moving more slowly than the anilides of known C_5 saccharinic acids. This, it is believed, has been done in the present work.

In all, 6 distinct spots (A-F) have been noted on the paper chromatogram, which might be considered as the anilides of C_6 saccharinic acids or higher. Three distinct fractions (C, D and E) have been isolated by fractionation on a cellulose column. Two of these are sirups, and one has a negative optical rotation. From the third fraction (C), a sirup of zero optical rotation, some crystalline material, m. 162-3°, has been isolated. The carbon-hydrogen analysis for this product is 54.05% carbon and 6.73% hydrogen. The values for C_6 and C_7 saccharinic anilides are 56.5 and 54.8% carbon, and 6.71 and 6.72% hydrogen resp. Thus the analytical data suggest a C_7 saccharinic anilide. Further analytical work on new material will be needed to confirm this.

Experimental

Twenty grams of D-xylose was dissolved in 40 cc. warm water, added to a solution of 50.2 grams of sodium hydroxide in 82 cc. water, a rinse of 10 cc. water added, and then 20 cc. of xylene as a surface layer to prevent oxidation by air. The solution, about 8 Normal in sodium hydroxide, was heated 10 hours in a steam bath (98-100°), then cooled, diluted to 1 liter with water, and this solution run thru a cation-exchange resin (IR-120) to remove the sodium ions. The acidic effluent reached a minimum pH of 2.5. The column was washed until the pH of the effluent rose to 4.0.

The total effluent (about 4 liters) was concentrated <u>in vacuo</u> to a thin sirup. It was dissolved in 100 cc. 95% ethanol, 40-50 cc. aniline added, and the mixture heated on the steam bath two hours. Then 50 cc. benzene was added, and the mixture heated 1 hour to distill off water azeotropically with the benzene. The solution was heated at 100° and 20 mm. until all remaining ethanol and benzene had been removed, then heated at 100° and 0.1 mm. to remove 25-30 cc. of unreacted aniline.

Chromatograms of the resulting red sirup showed the presence of two C_6, and one C_4 saccharinic anilide, also one or more fractions in the C_3 region. However the C_5 region was blurry (see A in figure 3) due to a strong interfering spot, which could be seen in visible as well as ultra-violet light. It was felt that this might be some unreacted saccharinic acid (lactic acid?). Attempts were made to remove it by reaction with a basic ion exchange resin, under conditions where the neutral saccharinic anilides would pass thru.

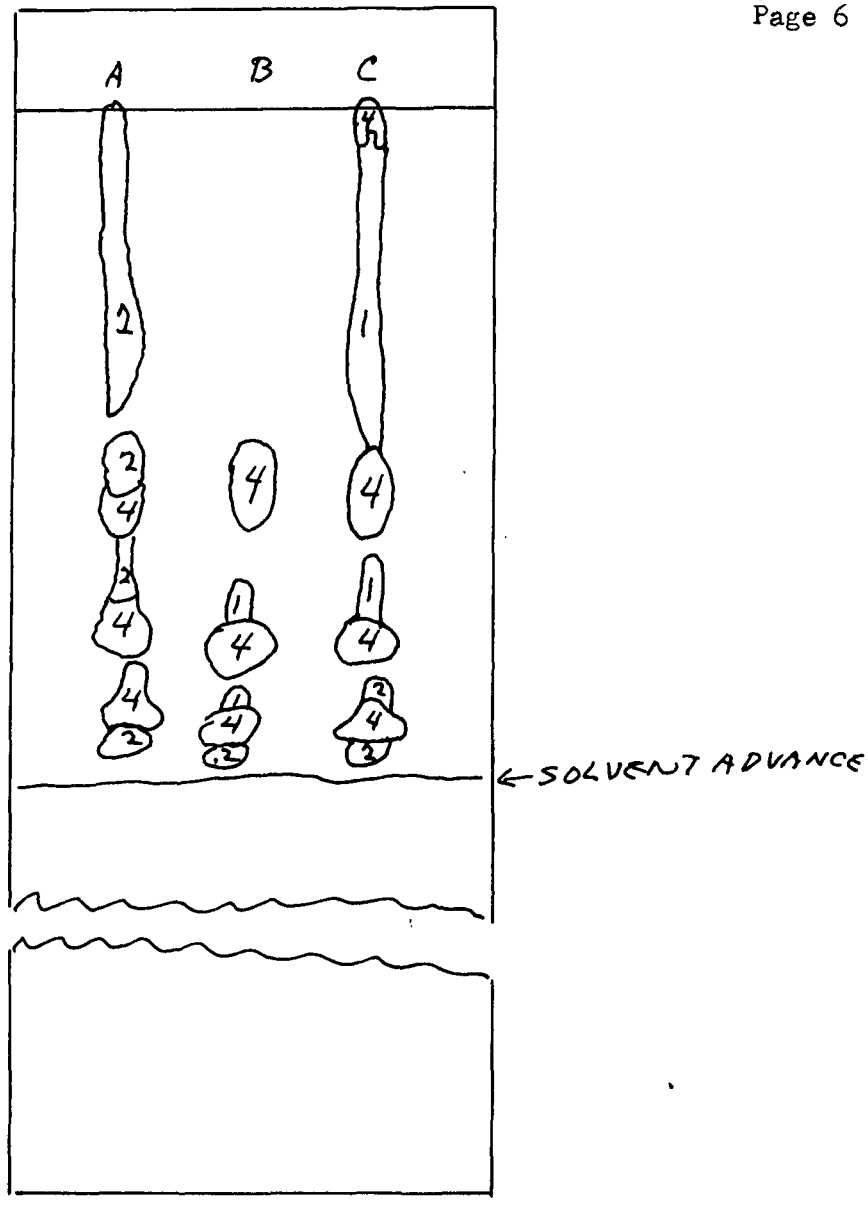

Figure 3

Resin Purification of Saccharinic Anilides

A=original mixture, B and C = mixture after treatment with Dowex-1 acetate and IR-4B acetate resins resp. Time = 2.5 hours, solvent = 30-1-20 acetone-water-benzene. Numbers denote intensity of spots from 1 = very faint to 4 = strong.

Use of a strongly basic resin (Dowex-1) in the OH form removed not only the interfering spot, but also the saccharinic anilides from a 50% ethanol solution. Apparently the resin was too alkaline and saponified the anilides.

The strength of the resin was then diminished by converting it from the OH or strongly basic form to the acetate form. This was done by washing the resin with 95% ethanol containing glacial acetic acid. Passage of an ethanol solution of the anilides thru this resin successfully removed the interfering spot (see B in figure 3).

On a larger scale a similar purification was used with some IR-4B resin in the acetate form. This resin is a weakly basic resin, in contrast to the Dowex-1 resin. The main reason for the switch to the IR-4B resin was a matter of supply; only a small amount of the Dowex-1 resin was available, in contrast to a large amount of the weaker resin. The interfering spot was also removed by the weaker resin. However there is a very faint zone above the C_5 region which was completely removed by the Dowex-1 resin but not by the weaker resin (compare B and C in figure 3).

A partial concentration of this slow zone occurred on the IR-4B resin column. The bulk of the anilides came thru in a dark red solution (about 2 liters) showing the pattern given in figure 3, and containing 18 grams of sirup. Some dilute yellow washings were then collected (about 400 cc. containing 3.5 grams sirup) which contained the bulk of the slow zone. Some C_5, C_4 and C_3 anilides were also present, but the

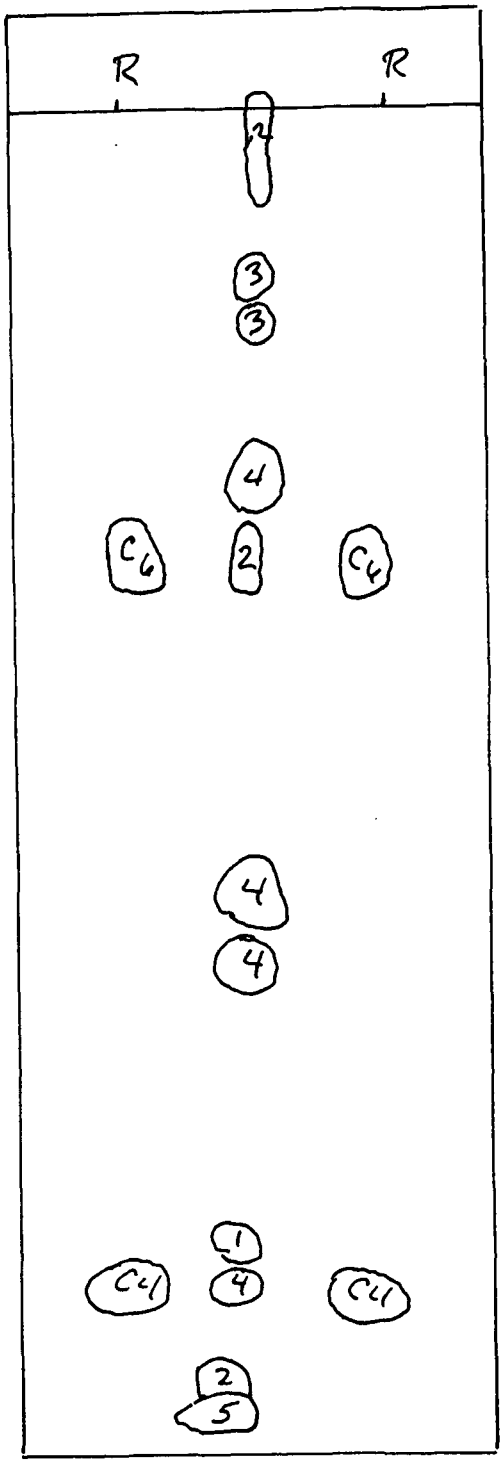

Figure 4

Slow Effluent from IR-4B Acetate Resin Column

C_6-reference compound is alpha-isosaccharinic anilide. Time = 2.5 hours, solvent = 30-1-20 acetone-water-benzene. Numbers denote intensities of spots from 1 = very faint to 4 = strong.

intensity of the slow zone was almost equal to that of the faster spots.

This slow zone consists of a series of 6 distinct spots (A-F). They are partially separated on the paper chromatogram when the solvent is allowed to advance to the bottom of the sheet (figure 4) and are completely resolved when the solvent is allowed to run beyond the end of the sheet (see figure 5).

The 3.5 grams of sirup was then fractionated on a 2 x 24-inch cellulose column. The eluting solvent was initially acetone containing 0.5% water, at a flow rate of 520 cc. an hour. The first 950 cc. of effluent was discarded. The next 830 cc. was taken in one fraction, and contained C_3, C_4 and C_5 anilides, as shown by a paper chromatogram. Fifty fractions of 52 cc. each were then taken, followed by fifty 104-cc. fractions. The solvent was then changed to acetone containing 1% water (1 liter, giving 10 fractions), and then to acetone containing 2% water (4 liters, giving 40 fractions). The nature of the various fractions was determined by spotting aliquots on a sheet of paper and running the chromatogram in the usual way. The results are given in Table 1. Fraction F remained on the column.

All of the combined fractions seem to be optically inactive, except 135-157 (anilide **E**). All are sirups, with the exception of 64-87 and 88-112. The former (impure C) has given about 11 milligrams of a crystalline material, which was recrystallized from ethanol-ethyl acetate to give 5 milligrams of material, m. 162-3°. The 88-112 fraction

(fraction C) has given about 25 mg. of a poorly crystalline material. The fact that 64-87 combined fraction gave crystalline material, and 88-112 did not leads to the suspicion that these fractions are both heterogeneous, despite the better purity shown by the latter on the paper chromatogram.

Analysis showed 54.05% carbon and 6.73% hydrogen (one determination). Calculated for a C_6 anilide, $C_{12}H_{17}O_5N$, 56.5% C and 6.71% H. Calculated for a C_7 anilide, $C_{13}H_{19}O_6N$, 54.8% C and 6.72% H. C_7 saccharinic acids or anilides are unknown at present.

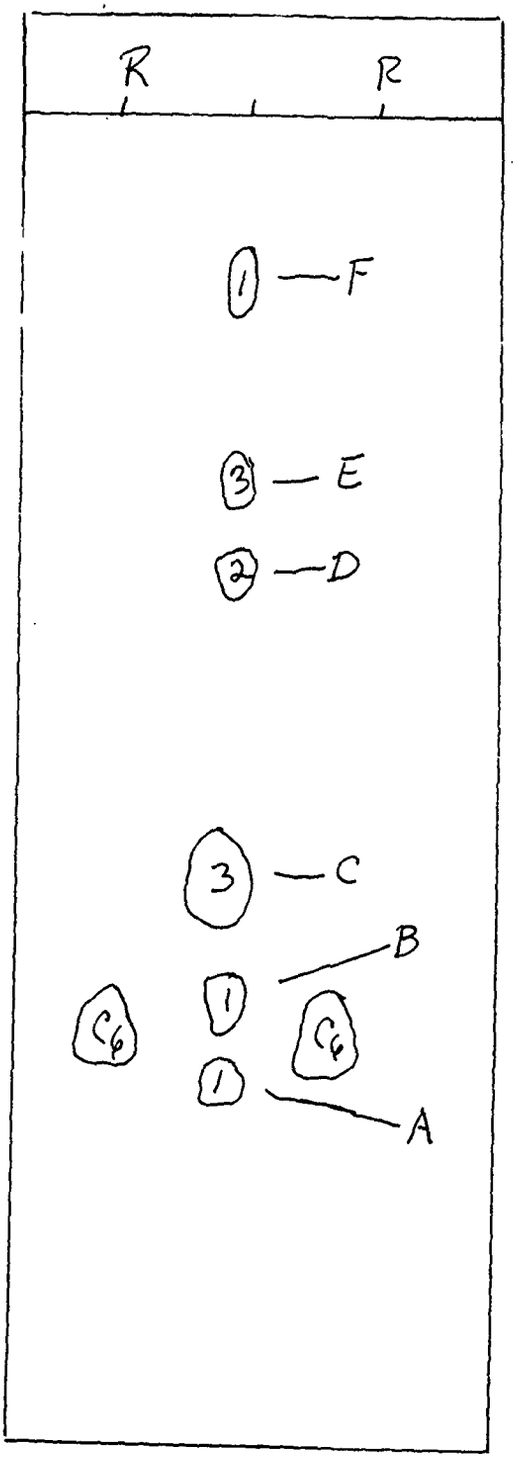

Figure 5

Higher-Carbon Saccharinic Anilides

C_6-reference compound is alpha-isosaccharinic anilide. Time = 24 hours, solvent = 30-1-20 acetone-water-benzene. Numbers denote intensties of spots from 1 = very faint to 3 = medium.

Table I

Fractions of Higher-Carbon Saccharinic Anilides

Obtained from a Cellulose Column

Fraction	Volume	Components	Weight	Remarks
0	830	C_3, C_4 and C_5	---	This was discarded
8-16	1250-1650	C_5		Discarded
40-56	2900-4050	C_5 and C_6-A and B		Discarded
64-87	4900-6450	mostly C_6-C	102 mg.	5 mg. crystals, m. 162-3°
88-112	6550-9900	C_6-C only	156 mg.	optically inactive sirup giving poor crystals
117-121	10400-10800	C_6-C and C_6-D	---	
122-126	10900-11300	C_6-D	30 mg.	optically inactive sirup
128	11550	C_6-C and C_6-E	---	
135-157	12300-14550	C_6-E	50 mg.	sirup, a = -15.6° in Ethanol

Note - a forerun of 950 cc. was discarded, also a volume of 830 cc. (fraction 0) containing C_3, C_4 and C_5 anilides. The main interest was in the fractions beyond the C_5 anilides.

Xylose is usually prepared from pentosan-containing materials, as corn-cobs, by acid hydrolysis, and the glucose present is removed by fermentation. The formation of only small amounts of higher (C_6) saccharinic acids might thus be attributed to hexose impurities present in the original xylose treated with alkali. However, paper chromatograms prepared from the xylose used in this work showed only one spot, and absolutely no trace of glucose as an impurity. A chromatogram of a known sample of xylose containing 2% of glucose as an added constituent showed a very definite spot in the glucose region. So it can be definitely stated that the xylose used in this work was pure.

References Cited

1. J. U. Nef, Annalen 376, 1 (1910).

2. J. C. Sowden and Dorothy Kuenne, J. Am. Chem. Soc. 75, 2788 (1953).

3. M. L. Wolfrom and J. N. Schumacher, ibid, 77, 3318 (1955).

4. Mary Grace Blair and J. C. Sowden, ibid, 77, 3323 (1956).

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FORMATION OF HIGHER-CARBON SACCHARINIC ACIDS FROM XYLOSE AND OTHER SUGARS

In Report No. 5 the formation of higher saccharinic acids from xylose was reported. These acids were isolated in small yield by conversion to the anilides and subsequent fractionation on an ion-exchange column and then on a cellulose column.

In the present work this formation of higher anilides has been repeated, starting with xylose as a starting material. From several of the fractions isolated it has been show that (a) these anilides can be converted to calcium salts and back to anilides again, (b) the original saccharinic acid mixture can be partially fractionated before anilide formation, showing that these higher acids are formed by the action of alkali, and not by the subsequent action of aniline on lower acids, and (c) periodate oxidation and subsequent paper chromatography shows the presence of fragments similar to those formed from the C_6-metasaccharinic anilides. Finally it has been shown that higher saccharinic anilides can be obtained by the action of alkali on glucose, galactose, and arabinose.

The original purpose of the present work was to prepare the alpha- and beta-C_5-metasaccharinic anilides from D-xylose as reference compounds for analysis of kraft black liquor. Both of these compounds have now been prepared in crystalline condition. The beta-anilide corresponds in melting point and optical rotation (but opposite in sign) to the anilide prepared

from L-arabinose (see Report No. 3). The alpha-anilide has finally crystallized, after six months in a sirupy condition. This product is new. The corresponding anilide prepared from L-arabinose (see Report No. 3) was obtained only in a sirupy condition.

Part of this work was presented before the Carbohydrate Division at the Atlantic City Meeting of the American Chemical Society.

One more fractionation of the higher anilides derived from xylose will be tried, to obtain enough material for a suitable carbon, hydrogen, and nitrogen analysis. Then this work will be written up for publication. The higher anilides are a side light of the main work, but are very interesting from the viewpoint of the formation of saccharinic acids. Now that some C_5 reference compounds have been obtained, the next stage will be a further identification of some of the many fractions present in kraft black liquor.

EXPERIMENTAL

Fractionation of higher anilides on a cellulose column.—A mixture of higher anilides, weighing 1.2 grams, was fractioned with acetone containing 0.5% water as a solvent. The forerun of 900 cc. and a zero fraction of 2500 cc., containing C_3, C_4, and C_5 anilides were discarded. Then 100-cc. fractions were taken, and later 250-cc. fractions. As the fractionation progressed, the water content of the acetone was gradually increased to 2%. The data for this run are given in Table I. It can be seen that there is very little optical activity in any of the fractions which may infer that these higher acids were formed by recombination of optically inactive C_2, C_3, and C_4 fragments. The weights of the several fractions are a little high,

as their total (1434 mg.) is greater than the weight of the original mixture (1200 mg.).

Fraction C crystallized partly to a sticky solid, and from this mixture, with the aid of ethanol and ether, some solid was obtained. This is a repetition of the results given in Report No. 5 and shows that this preparation of higher anilides is a reproducible experiment.

Proof that the higher anilides are actually anilides of organic acids.—Some doubt has been felt as to the exact nature of the higher anilides. They are mostly sirupy materials giving nonfluorescent spots on a paper chromatogram, similar to the behavior of known saccharinic anilides. The slowness of travel on the chromatogram might be attributed to a difference in the organic amine portion of the several fractions, rather than to the acidic portion. The following experiment is therefore reassuring.

A part of fraction C_6-E, 50 mg. of a sirup, was refluxed in water with some Amberlite IR-120 cation-exchange resin for one hour to effect hydrolysis of the amide linkage. The acidic solution was neutralized with lime to pH 10 (heating in part) and the excess lime precipitated with carbon dioxide. The solution was concentrated to a small volume and ethanol added. A precipitate was obtained, which was washed with ethanol and ether to give 9 mg. of a white powder, presumably the insoluble calcium salt of the higher saccharinic acid.

TABLE I

FRACTIONATION OF HIGHER ANILIDES ON A CELLULOSE COLUMN

Fraction	Volume of Effluent Liters	Weight, mg.	Specific Rotation in Ethanol
C_3, C_4, C_5	0-2.5	(846)	—
A and B	3.2-4.1	—	—
B and C	4.4-4.8	—	—
C	4.8-7.2	235	+3°
C and D	7.2-8.4	—	—
D	8.4-10.0	35	+6°
D and E	10.0-11.4	—	—
E	11.4-15.5	110	-4°
F	15.5-18.9	24	0°
F and F'	18.9-19.5	—	—
F'	19.5-21.7	10	—
Total fractions		435	
Mixed fractions		153	
C_3, C_4, C_5 fractions		846	
Total recovery		1434	

This salt was dissolved in water and the solution passed through an IR-120 cation-exchange column to give a solution of pH 3.2. An aliquot of this solution, equivalent to 4 mg. of the salt was concentrated in vacuo to dryness, 0.05 cc. freshly distilled aniline added, then 0.5 cc. ethanol and the mixture heated 2 hours under reflux. This solution gave no spots on a chromatogram. So it was heated with more aniline in an open beaker on a steam bath 2 hours. The dark brown residue then gave a definite spot on a paper chromatogram similar to that for the original C_6-E fraction.

So it can be definitely said that this higher anilide can be hydrolyzed to a free acid, then converted to an ethanol-insoluble salt, back to the free acid and to the original anilide again.

Proof that the higher saccharinic acids are formed during heating with alkali and not during heating with aniline.—Presumably the higher saccharinic acids are formed by condensation of smaller units, but it is possible that this condensation might take place during the formation of anilides, by the action of hot aniline. This possibility has been ruled out by the partial fractionation of the acid mixture into higher and lower acids before anilide formation.

A mixture of saccharinic acids was obtained by heating 30 g. of xylose in 8 N NaOH by the standard procedure. The resulting sirup was converted by extraction with varying mixtures of ether and absolute ethanol into four fractions. The data are given in Table II. The ether soluble fraction was a very fluid light yellow liquid, whereas the 1-1 ether-ethanol fraction was a dark red viscous sirup. The intermediate fraction B ressembled fraction A, the fluid liquid.

One-gram portions of fractions A and C were each heated with 2 cc. aniline, 2 cc. glacial acetic acid and 50 cc. ethanol for 1-2 hours on a water bath, the ethanol slowly distilling. The mixture was then heated at 1 mm. and 100° to remove the acetic acid and most of the aniline. The remaining sirup in each case was dissolved in 20 cc. ethanol and run through an IR-4B-acetate form anion exchange resin (10 cc. volume, wet with 50% ethanol). The resin was washed with 95% ethanol, the effluent being collected in two portions, (140 cc. and 170 cc. volume) for each mixture.

The four effluents (A-1, A-2, C-1, and C-2) thus obtained were decolorized and concentrated to sirups. The weights of sirup were 1.20 grams and 0.037 gram for A-2 and A2 and 1.20 grams and 0.021 gram for C-1 and C-2.

Each of these four sirups was spotted on paper and the usual chromatogram run in 30-1-20 acetone-water-benzene. As shown in Figure 1, the anilide A fractions gave spots only for C_3, C_4, and C_5 saccharinic anilides, whereas the anilide C fractions gave anilides in the higher or slower regions. So the fractionation of the original mixture of acids with ether and ethanol has persisted through the anilide formation. Hence, the anilide formation has no effect on the formation of higher saccharinic acids.

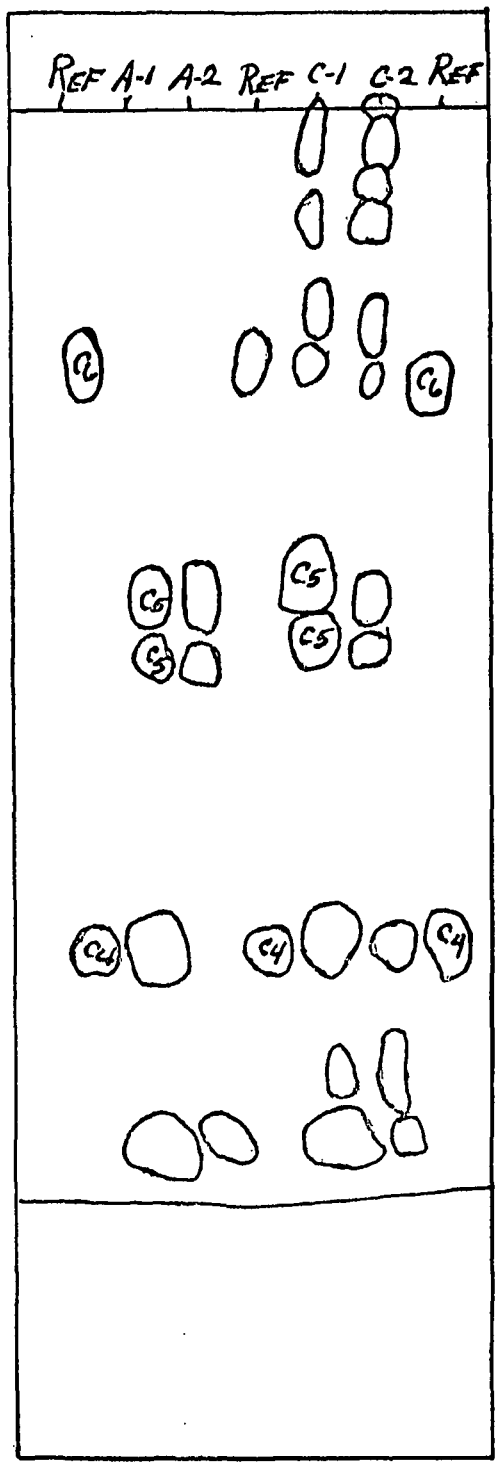

Figure 1

Chromatogram showing fractionation of higher and lower saccharinic acids before anilide formation (run 4 hours in 30-1-20 acetone-water-benzene)

TABLE II

ETHER-ETHANOL FRACTIONATION OF HIGHER ACIDS

Solvent Mixture		Weight of Fraction, grams
Absolute ether	(A)	11.50
5-1 ether-ethanol	(B)	8.6
1-1 ether-ethanol	(C)	6.5
Absolute ethanol		0.0
Insoluble in ethanol		1.39
Total		28.0

Ash content of calcium salts of higher saccharinic acids.—Several higher anilides (15-50 mg.) were dissolved in 2 cc. ethanol and 5 cc. water, 0.2 g. IR-120 cation-exchange resin added, and the solutions heated 16 hours in a steam bath, then 1 hour in a boiling water bath. Each solution was filtered from the resin and titrated to pH 11 with saturated lime water at 60°. The excess lime was precipitated with carbon dioxide. The filtrates were concentrated in vacuo at 50° until a precipitate formed ($Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$). The solutions were filtered, concentrated to 0.5 cc. and ethanol added to give a precipitate of the calcium salt.

Each of these calcium salts was ashed to determine the calcium content. The results were not too encouraging. Perhaps the salts still contained some calcium carbonate. The data are given in Table III. It was hoped that the calcium carbonate would show a definite decrease from fraction D to E to F as the rate of movement on the sheet decreased or the molecular weight increased.

TABLE III

ASH CONTENTS OF CALCIUM SALTS

Anilide Fraction, mg.		Calcium Salt mg.	% Yield	Sulfated Ash
C_6-D	17.5	7	40	45.9
C_6-E	43	17	40	27.3
C_6-F	22.5	6	27	34.9

Note: The calculated yields of calcium sulfate from the calcium salts of C_6, C_7, and C_8 saccharinic acids are 34.0, 29.6, and 26.2%, respectively.

Periodate oxidation of higher anilides. Oxidations were carried out with 2 mg. each of fractions D, E, and F, in 0.5 cc. water and 20 mg. sodium metaperiodate at 0° for 0 hour. The solutions were then treated with a little 10% ethylene glycol in water to destroy excess periodate and then concentrated to dryness. The residue in each case was dissolved in acetone and this extract concentrated to dryness. The new residue was dissolved in 0.10 cc. ethanol and 0.01 cc. spotted on paper. The chromatogram was run 4 hours in 30-1-20 acetone-water-benzene. The reference compound run was the oxidation mixture from a periodate oxidation of alpha and beta glucometasaccharinic anilides.

As shown in Figure 2, a series of four spots resulted in each case, 3 in the C_4 region and a faint spot in the C_3 region. This pattern is similar to the pattern of spots obtained from the reference mixture, so it can be concluded that there is some similarity in structure of the higher anilides to the C_6-metasaccharinic anilides.

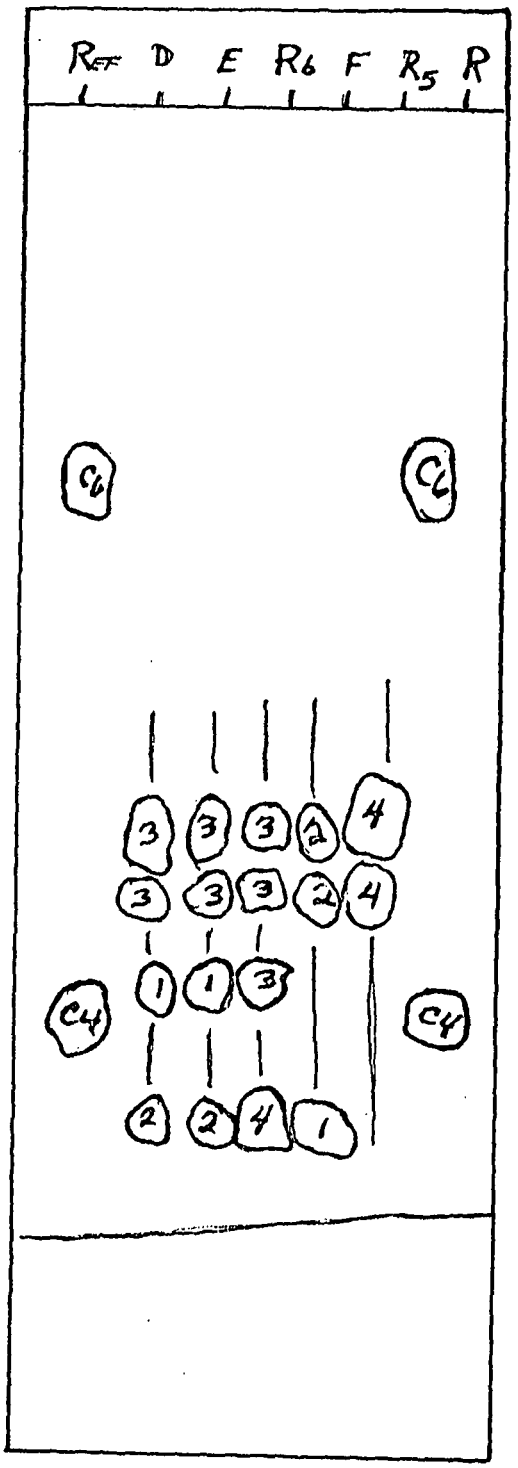

Figure 2

Chromatogram of fragments obtained from higher anilides by periodate oxidation.

R_5 and R_6 are fragments similarly obtained from C_5 and C_6 metasaccharinic anilides. (run 5 hours in 30-1-20 acetone-water-benzene)

Numbers 1-4 = very faint, faint, medium and strong for intensity of spots.

Formation of higher saccharinic anilides from other sugars.--Experiments were carried out with glucose, galactose and arabinose in a similar manner as with xylose. The anilide mixtures were partially fractionated on an IR-4B-acetate column and chromatograms run (see Figure 3). It can be seen that higher anilides are formed in all cases. For each of the four sugars there are two zones of 2 spots each above the C_6 region. In the case of the galactose mixture there is a pair of very faint spots between the two zones. In the case of the two hexose mixtures there are two pairs of slower spots near the starting line, in contrast to the pentose mixtures. It might be concluded that these pairs represent alpha-beta isomers of C_6, C_7, C_8, etc. anilides.

Isolation of alpha and beta C_5-metasaccharinic anilides derived from xylose.--Fractions containing the beta anilide obtained from various column fractionations were combined and crystallized from ethyl acetate. The product obtained after two crystallizations was still slightly impure, with a melting point of 113-114° and a specific rotation of $(\alpha)_D^{24} = -46°$ (c 4, 95% ethanol). This isomer crystallizes very readily and moves more slowly on the paper chromatograph than does the alpha isomer. The data for the L-beta anilide, obtained from L-arabinose (see Report 3) were m.p. 119-120° and a specific rotation of +49°.

The alpha isomer originally was obtained as a sirup and finally crystallized after standing for six months at room temperature. It has been crystallized from the minimum of ethyl acetate to a melting point of 96-97°. The specific rotation is $(\alpha)_D^{24} = +24°$ (c 1, 95% ethanol). It cannot be

compared with the corresponding L-isomer prepared from L-arabinose, as this latter (see Report 3) was a sirup.

Both of these compounds have been shown on paper chromatograms of anilides of kraft black liquor saccharinic acids. Now it should be possible to isolate these as crystalline products from such mixtures.

Remarks concerning fractionation on cellulose columns.--A new type of cellulose column, a Grycksbo column made in Sweden, has been tried with poor results. This consists of a roll of paper tightly encased in a polyethylene cylinder. It does not seem to work as well as a glass column packed with cellulose powder. This poor performance was confirmed by Messrs. Talbot and Balston of Balston Ltd. of England, who were visiting at the Institute this last week (February 22, 1957). So future work will be confined to glass columns.

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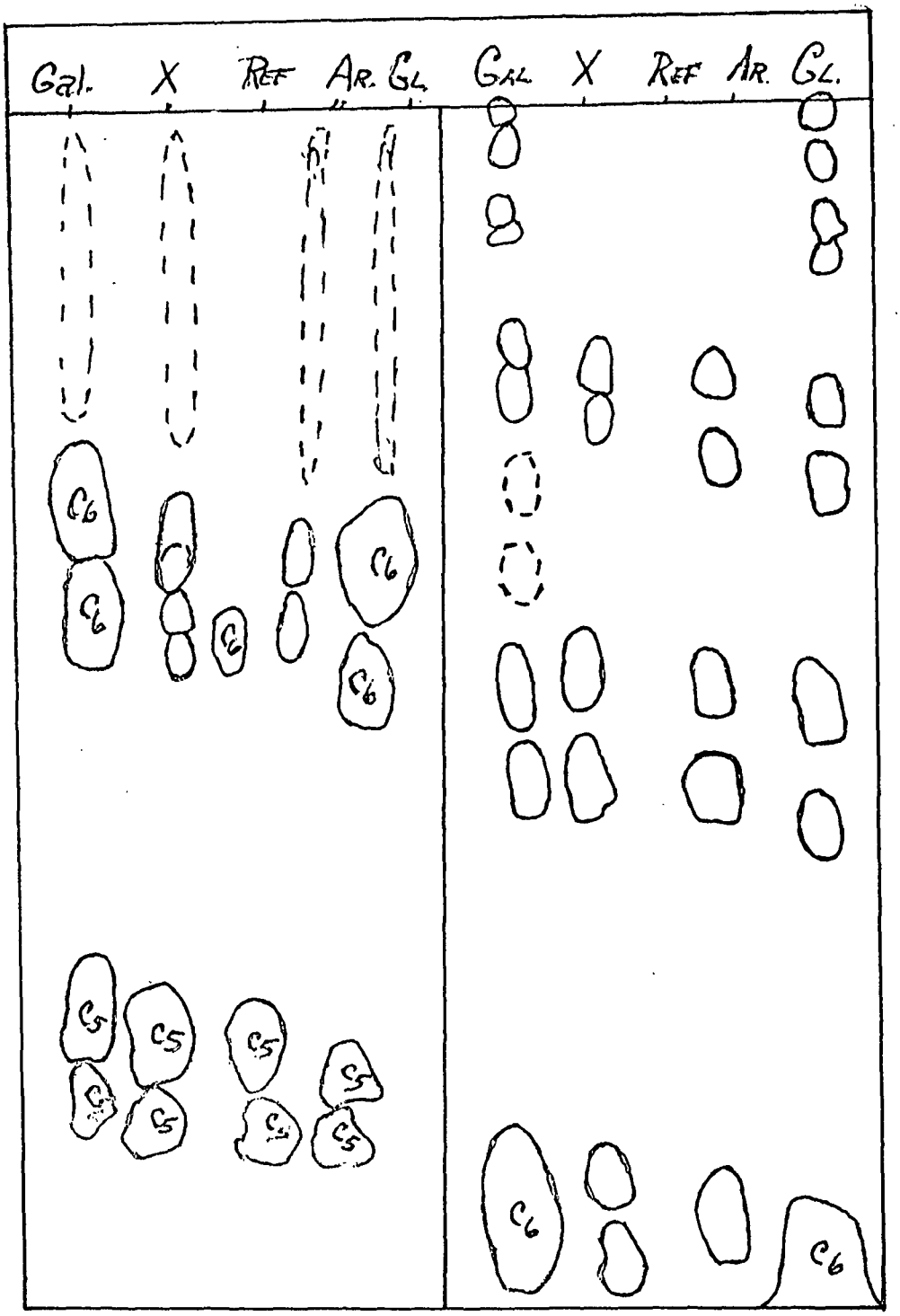

Figure 3

Paper Chromatograms of Higher Saccharinic Anilides
(run in 30-1-20 acetone-water-benzene mixture)

The left chromatogram shows the C_5 and C_6 regions and many overlapping spots above. In the right the solvent has been allowed to run further, so that the higher anilides above the C_6 region are resolved.

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VARIOUS METHODS OF PREPARING CELLULOSE COLUMNS AND SOLVENT COMBINATIONS FOR FRACTIONATION OF SACCHARINIC ANILIDES

In this report two problems have been studied. First various methods of preparing cellulose columns were tried, and it was found that the sedimentation method is the best. Secondly various combinations of acetone and ligroine were used in the fractionation of saccharinic anilides. It was found that a 70-30 mixture of acetone-ligroine was effective in separating the C_5 saccharinic anilides, and that mixtures containing more ligroine (up to 70%) were effective in separating the anilides of lower molecular size. This new technique has been tested with relatively simple mixtures of saccharinic anilides derived from xylose and will now be applied to the more complex mixtures obtained from kraft black liquor.

EVALUATION OF CELLULOSE COLUMNS

Cellulose columns were prepared by three methods, listed below and of these three, the method of sedimentation packing was found to be the most uniform. The uniformity of packing was determined by running a band of dye down the column and noting the presence or absence of skewing or stabbing.

Sedimentation packing. This method consists essentially of allowing a slurry of cellulose powder in 50% aqueous acetone to settle in a glass column to form a uniform bed. As shown in Figure 1, the column consists of a glass tube, 2 x 22 inches, sealed at the lower end to a 10/30 inner ground joint, and at the other end to a 50/60 outer joint. An extension tube, 30 inches in length, is coupled to the upper part of the column to allow a greater length and volume of liquid during the sedimentation.

The bottom of the column is first fitted with a 30 mm. perforated filter disk, a thin layer of glass wool and then a 15 mm. layer of sand. This arrangement prevents any fine cellulose powder draining from the column.

The column and attached extension tube are then filled with a mixture of 1-1 acetone-water (de-aerated at 20 mm. and room temperature). The solution is added slowly so as not to disturb the level surface of the sand bed. Then a slurry of Whatman No. 1 cellulose powder in 1-1 acetone-water is made up by (a) stirring violently with a Lightnin' mixer for 5-10 minutes and (b) de-aerating for 5-10 minutes in a filter flask at 20 mm. and room temperature. This slurry is added to the top of the column in 200 cc. portions and the powder allowed to settle. During the sedimentation the liquid is drained from the column at a slow rate (150 cc. an hour), controlled by a capillary attached to the 10/30 ground joint.

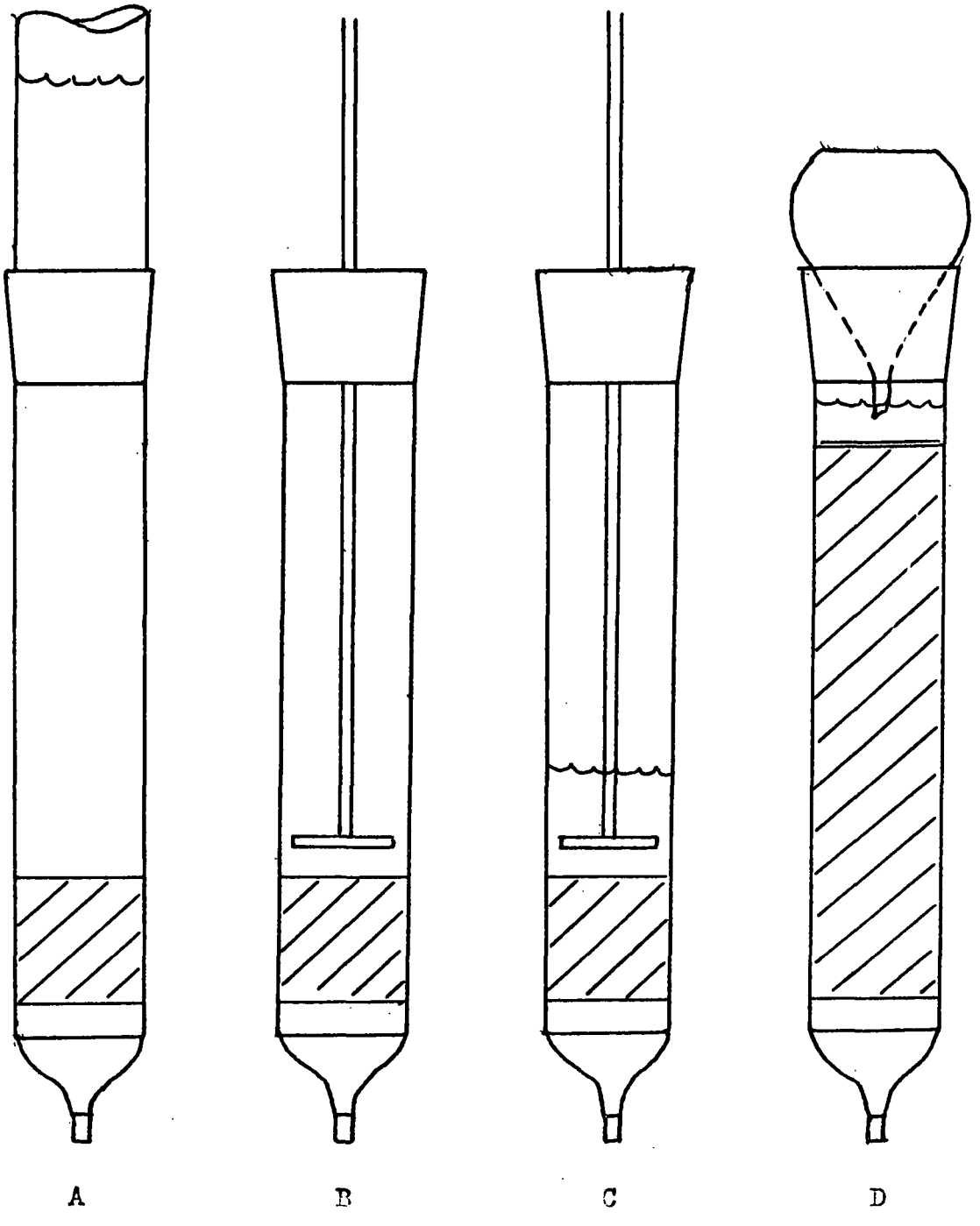

Figure 1

Preparation of Cellulose Columns

A. Sedimentation type
B. Dry Packing
C. Wet Packing
D. Column in operation

After some of the powder has settled to form a 2-inch bed in the column, the restricting capillary is removed, and the column will now drain at a rate of about 1 liter an hour. As the liquid level in the column falls, fresh slurry is added, until a bed is obtained with a height just below the 50/60 ground joint in the lower column. The liquid and slurry in the upper tube are removed through a side tube, and air pressure (5 pounds/sq. in.) applied to the liquid remaining above the cellulose powder. This compresses the cellulose bed about an inch in height. It is desirable to have the final height of the bed about two inches below the ground joint.

A filter paper cut to fit just inside the column is then placed on top of the bed. A certain level of liquid is always maintained above the bed, and when the column is not in use, the upper ground joint is closed with a glass stopper.

Dry packing. This is the style of packing used in the earlier phase of this project. The bottom of the empty column is fitted with a perforated plate and glass wool, then dry cellulose powder is poured into a height of 1-2 inches. The column, held vertically, is tapped on the sides to cause even settling, and then the powder compressed from above with a rammer, either a metal plate on the end of a brass rod, or a cork fastened to a wooden dowel. This compression is done as strongly as possible, without breaking the glass tube. This requires a little judgement on the part of the operator.

Then another portion of powder is added, and the compression repeated. In this way the column bed is gradually built up, section by section. Finally solvent is added to the dry column. This is best added from the lower end, to displace upward any air from the column. A funnel and a long rubber tube are used in this operation. A piece of filter paper is placed on the upper surface of the cellulose bed and the column is then ready to operate.

Wet-packing. This is carried out in the same manner as dry-packing except that the powder is added in the form of a de-areated slurry. The liquid (1-1-acetone-water) is allowed to drain freely from the bottom of the column. As the compression of the liquid slurry increases, the flow of liquid will slow down. In fact, the operator can almost control the flow rate by the force of compression. A desirable rate here is about 200-400 cc. an hour.

To obtain a level upper surface to the cellulose bed by this style of packing, the author has found it advisable to let the last portion of slurry settle without compression with a rammer. A final compression with air (5 pounds/sq. in.) may be used above the liquid level.

Comparison of weight of cellulose in the columns. The amount of cellulose powder used in the sedimentation packing was 240-260 grams per column, whereas the wet- and dry-packed columns held 350-370 grams. Thus the compressive styles of packing give a tighter and less bulky bed than does the free sedimentation.

Flow rate in the columns. Each column was washed with 50% aqueous acetone (about 1-2 liters) and then acetone containing 0.5% water, and finally with acetone containing 0.5% water and 10% ligroine (b. 60-90.). The rate of flow for the sedimentation packing was 1700 cc. an hour, whereas the two compressed packings had much slower flow rates of about 400 cc. an hour. All these flow rates were unchecked by capillary restrictions. In actual fractionations flow rates are generally restricted to 100-150 cc. an hour in most cases, for all styles of packing. Some workers (as E. Merler) who advocate the wet-packed column, feel that a cellulose column is most effective when the flow rate is unchecked, so that solvent will not back up in the column due to a constriction at the bottom.

Eveness of dye flow. In each case the liquid level in the column was allowed to fall to the top of the bed. The flow was then stopped and 5 cc. of acetone, containing 5 mg. of Sudan IV dye, added carefully to the top of the bed. This was done slowly with a medicine dropper or pipet, the dye solution being applied to the center of the covering filter paper, and never to the edges or the glass walls. The solution will then form a uniform liquid layer about 5 mm. in height above the bed surface.

This liquid is allowed to remain stationary for 1-5 minutes, so that the color diffuses partly into the cellulose. Then liquid drainage is started at a very slow flow-rate, about 20-30 cc. an hour, by use of a capillary at the bottom of the column. When the last of the dye solution just enters the top of the bed, about 2 cc. of solvent (acetone-water-ligroine) is added as a rinse. Several more rinses are added similarly, so that all of the dye is washed into the bed. When the upper edge of the dye band is about 2 cm. below the upper edge of the bed, a considerable amount of solvent is added, to a height of 2 inches. Then a fountain containing 500 cc. or more of solvent is placed on top of the column, and the liquid flow changed to a faster rate of 100-150 cc. an hour, by use of a different capillary.

The most suitable dye movement was with the sedimentation type of packing. The band moved in a uniform manner down the column, broadening because of diffusion to a width of 4-6 cm., but it was always horizontal with no stabbing or irregular flow. The wet and dry-packed columns gave irregular dye bands, often with quite serious stabbing. This stabbing seemed to occur wherever a boundary existed between the several packing zones. In other words, the sedimentation type of packing was continuous, whereas the other two types consisted of a series of zones, and the interfaces between these zones seemed to interfere with the solvent flow.

The wet- and dry-packed columns are denser than the sedimentation type are therefore may have a greater capacity for separation than the sedimentation type. However, the greater uniformity of packing for the latter type, despite its lighter packing and faster flow, seems to make it the most desirable type to use. It is interesting that a booklet on column chromatography, put out by Merck and Company recommends the sedimentation type of packing and does not even consider any other method.

EVALUATION OF SOLVENT MIXTURES ON CELLULOSE COLUMNS

In earlier work on this project the solvent used for fractionation of saccharinic anilides on cellulose columns was acetone containing 0.5% of water. It was found that if the water content was increased to 5-10%, the anilides were rapidly washed from the column and no fractionation occurred. Thus in the fractionation of "higher" saccharinic anilides derived from xylose (see Report No. 6, Feb. 1957), a solvent containing 1-2% water was used to speed up the movement of these slow-moving fractions from the column in an orderly fashion.

In the present work it was desired to slow down the movement of the C_3, C_4 and C_5 saccharinic anilides in order to obtain a better separation. As shown in Report No. 4 (Figure 3), at least 4 C_5 and 2 C_4 fractions are obtained from kraft black liquor, as shown on a paper chromatogram. Attempted fractionations on a cellulose column were not successful, these fractions moving too rapidly through the column.

In the present work various solvent mixtures containing increasing amounts of ligroine were used to fractionate known mixtures of C_3, C_4 and C_5 saccharinic anilides derived from xylose rather than benzene. Benzene is being used to slow down the movement of the various anilides on paper chromatograms. However it is

Footnote: "Column Partition Chromatography" by Nelson R. Trenner, 1957, Merck and Co. Inc., Rahway, N. J."

felt that with the use of large amounts of solvent on a cellulose column, that ligroine would be a better solvent than benzene, from the viewpoint of toxicity of the vapors.

Preparation of xylose saccharinic anilides. This preparation (93) was made in the usual way (see Report No. 6), by treating xylose with hot 8 N NaOH, removing the sodium ions with a cation-exchange resin, heating the sirupy acids (25.5 grams) with an excess of aniline and acetic acid, then passing the product through a buffered IR-4B-HOAc column to remove unreacted acids. The resulting sirupy product, a mixture of saccharinic anilides, weighed 26.0 grams, corresponding to 27.4 grams of xylose as the starting material. This yield is believed low, and is probably due to a low conversion of lactic acid to the anilide.

This mixture contained C_3, C_4 and C_5 saccharinic anilides predominantly, with small amounts of C_3A, a material moving on the paper chromatogram between the C_3 and C_4 regions, and three fractions, between the C_4 and C_5 regions, termed C_4A, C_4B and C_4C. C_4B was present in very small amount. In addition, it was found that the slower solvents tested below, containing more ligroine, fractionated the C_3 fraction into two equal parts, one of which was crystalline acetanilide, and the other sirupy lactic anilide. A typical paper chromatogram of the mixture is shown in Figure 2.

Fractionations on the cellulose column. In each case a sedimentation type of packing was used in a 2 x 22-inch column. The flow rates were normally about 100-150 cc. an hour. In some cases where the column was run overnight, a reduced rate of 30 cc. an hour was used. The amount of sirupy anilide mixture used in each run was 1.0 gram, equivalent to 1.05 grams of xylose originally.

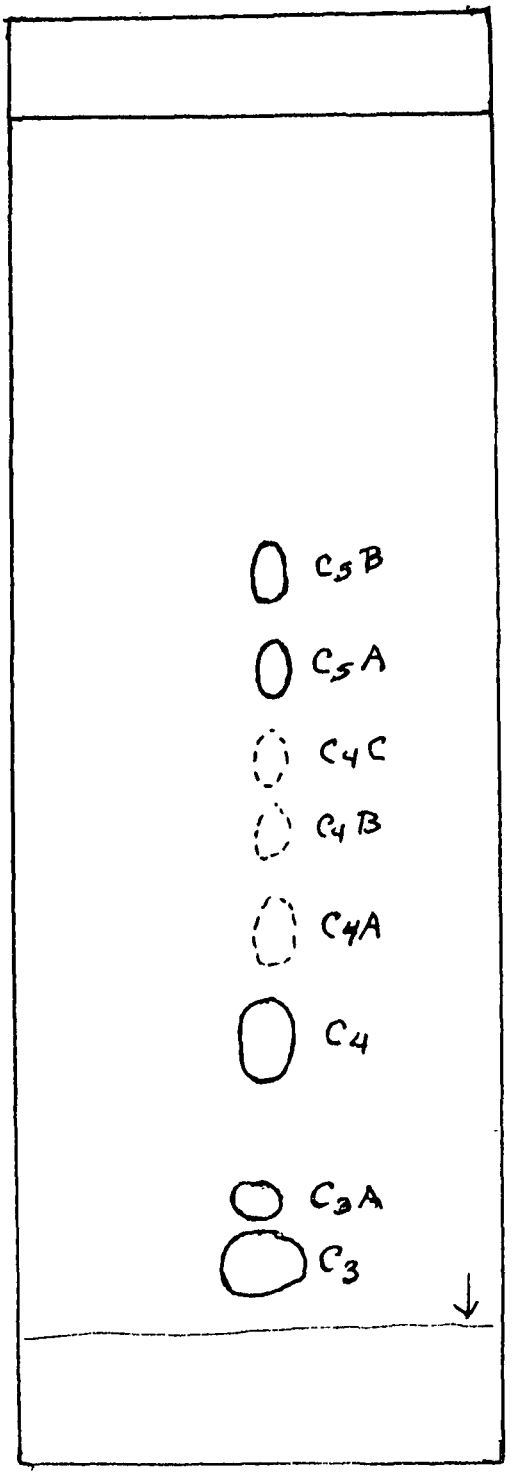

Figure 2

Paper Chromatogram of Saccharinic Anilides
Derived from Xylose

Mobile Solvent - 30_1_20 acetone-water-benzene
Time of run - 5 hours

About 0.8 mg. of Sudan IV dye was added to the sirup to serve as a marker of the solvent flow down the column. This dye emerged from the column after a liquid flow of 500-600 cc. and generally preceded the fastest fraction (C_3). In some cases the dye and the C_3 fraction moved at the same rate. The volume of liquid preceding the dye, termed the fore-run, was discarded, and then fractions were collected, ranging from 25 to 100 cc. in volume.

The total volume of effluent required to remove the slowest fractions (C_5B) ranged from 1500 to 5600 cc., the amount being roughly proportional to the concentration of ligroine in the acetone. (See Table I and Figure 3).

Fractionation with acetone alone. This solvent contained 0.5% water, as did all the mixtures below, where solubility allowed. The results are shown in Table I, four main fractions being taken, for a total recovery of 733 mg. out of 1000 mg. added. No attempt was made to isolate various mixed fractions of C_3 and C_3A, and of C_4A, C_4B and C_4C. The separation of C_5A and C_5B seemed to be fairly good, only a small amount of mixture being obtained. No pure C_3A, C_4A or C_4C were obtained.

Fractionation with acetone and 10-30% ligroine. Three experiments were carried out with a mixture of acetone containing 10% ligroine, at rates of 100, 140 and 30 cc. an hour. (95, 99, and 101). The fraction moved through the column more rapidly at the 30 cc. rate than at the other rates. However, at the higher rates the movement of fractions was slightly slower than with the acetone alone (see Figure 3). The fractionation in all three cases was better for the C_3A and C_4A and C_4C fractions, some of these being obtained in relatively pure form.

TABLE I

FRACTIONATIONS ON CELLULOSE COLUMN

Expt.	Solvent	Flow Rate cc./hr.	Vol. Solvent Used after fore-run	C_3' mg.	C_3 mg.	C_3A mg.	C_4 mg.	C_4A mg.	C_4C mg.	C_5A mg.	C_5B mg.
94	Acetone	100	2500	238			179			118	198
95	90-10 mixture	100	3000	211		64 impure	281			136	190
99	90-10 mixture	140	2800	216			351			121	268
100	90-10 mixture	140	2900	272		30	406			140	214
101	90-10 mixture	30	1500	291		52	325			105	195
102	70-30 mixture	140	3800	236		61	229	53	73	114	209
104	600 cc. 30-70, then 70-30 mixture	140	2750	118	100?		234			189	151
105	1000 cc. 50-50, 1000 cc. 60-40, 2000 cc. 70-30	140	3500	245			243			111	202
108	3000 cc. 30-70 then 70-30 mixture	600 cc. at 30, 1650 at 140, 520 at 30, then 140	---	97	128	37	---			---	---
109	3000 cc. 30-70 (half-sat'd. with water), then 70-30		5600	84	121		---			121	192
Average yield, mg. anilide				100	110		281			128	202
Average yield, calcd. as acid					60		173			85	135
Yield acid per 1.00 g. xylose					57		165			81	128

Note--In runs 94-102 and 105 the yields under C_3' actually represent yields of C_3' and C_3, no separation being achieved.

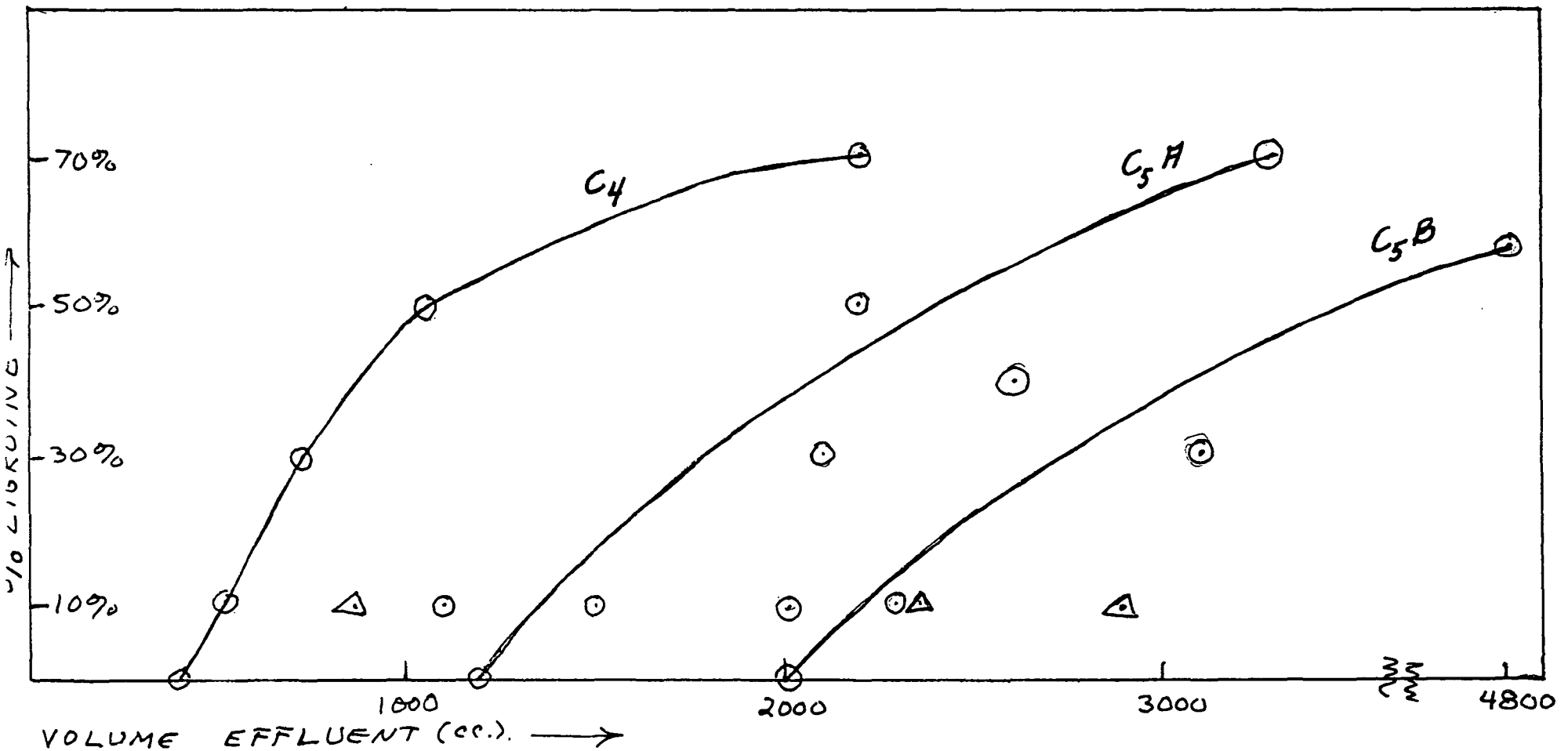

FIGURE 3

VARIATION OF PEAK EFFLUENT VOLUMES WITH LIGROINE CONTENT OF SOLVENT

⊙ - NORMAL CELLULOSE POWDER

△ SWOLLEN " "

Experiment 100 in Table I represents a column packed with a modified cellulose. This was prepared by dispersing the Whatman No. 1 powder in 17.5% NaOH for 5 minutes, then diluting with water, and acidifying with acetic acid. The cellulose precipitated out again (it is probably not a cellulose powder but a hydrocellulose) and was washed thoroughly with water and acetone and air-dried. The material, when packed in a column, had a flow rate similar to that for the original cellulose, but the various anilides mov d through the column at a slower rate (except for C_5B, see Figure 3) than in the case of the original cellulose powder. Due to the difficulty of making this swollen cellulose in a reproducible manner, it was abandoned.

With acetone containing 30% acetone (expt. 102) a still better fractionation was obtained, with relatively large amounts of C_4A and C_4C being obtained in pure form. These are still sirups, with specific rotations in ethanol of -3.7° and $+11.3^\circ$ resp. These, being optically active, may be isomeric C_5 anilides, and of the type noted earlier in chromatograms from black liquor.

Fractionation with acetone containing 70% ligroine. Several experiments were tried with mixtures containing 70% acetone. One difficulty with this mixture was the low solubility for water. A saturated solution, containing about 0.3% water, was used. This smaller amount of water may affect the partition of the anilides between the water phase on the cellulose and the mobile solvent.

In the first experiment (104) the 1 g. of sirup was dissolved in 3 cc. of a 70-30 acetone-ligroine mixture, and added to a column which had been washed first with a 30-70 mixture of acetone-ligroine. The solution was washed into the column with more 30-70 mixture, but part of the sirup seemed to precipitate out on the column in an irregular manner, and a very ragged dye band resulted.

The column was washed with 600 cc. of 30-70 mixture, then with 50 cc. each of 40-60, 50-50, 60-40 and finally with about 3 liters of 70-30 mixture. The fractionation was not too effective, probably due to the poor addition of the solution to the column. This is noted for the C_5A and C_5B fractions, the values being out of line with other runs. However here for the first time a separation of the C_3 fraction into two fractions, the first being acetanilide, was achieved.

In the second experiment (105) the column was first washed with a 50-50 mixture, and the sirup in 2 cc. of acetone applied to the top of the cellulose bed. This was rinsed in with 2 cc. portions of 70-30, 60-40, and 50-50 mixture. The column was then washed with 1 liter each of 50-50 and 60-40 and finally with 2 liters of 70-30 mixture. This fractionation was more successful, the dye band moving smoothly and a good separation of C_4 and C_5 fractions resulted. Fraction C_3 however came through as one fraction, so the 50-50 mixture did not slow up these components as well as did the 30-70 mixture. No effort was made here to isolate the C_4A or C_4C fractions.

A third experiment was tried, starting with 3 liters of 30-70 mixture and then shifting to a 70-30 mixture, trying to combine the best parts of experiments 104 and 105. The dye band moved smoothly, the solution being applied as in 105. A good fractionation was obtained for the C_3 and C_3A fractions, this being accomplished with the 30-70 mixture. However the shift to the 70-30 mixture was rather disastrous, as the C_4 and C_5 fractions came through together without separation. Apparently the fault lay with using a 30-70 mixture saturated with water (suggestion by E. Merler). Probably some water separated from this mixture, was absorbed by the cellulose, and then picked up subsequently by the 70-30 mixture. This last solution, containing a large excess of water, could easily wash the water-soluble C_4 and C_5 anilides rapidly off the column.

So the final fractionation (109) was carried out with three liters of 30-70 mixture, half-saturated with water. The subsequent transition to 70-30 mixture was successful, and a fractionation of everything from C_3 to C_5 saccharinic anilides was effected, the volume of effluent being spread over a range of 5600 cc.

Conclusions regarding solvent mixtures. The several experiments show that a 70-30 mixture alone can be used for fractionation of C_4 and C_5 saccharinic anilides, but that use of some 30-70 mixture first will separate some of the faster fractions. Use of a 50-50 mixture initially will not do this.

However shifting from one solvent to another requires several hours of close attention by the operator and is a bit tedious. The 50-cc. portions of solvent used between the two mixtures are added at half-hour intervals approximately and this cannot be done automatically. Perhaps in the fractionation of kraft black liquor mixtures two runs can be made, one of the faster fractions with 30-70 mixture, and another run with a 70-30 mixture to separate the slower components. This may be easier than trying to separate all the components in one operation.

Precision of fractionations. From the data in Table I it can be seen that the yields of C_5A and C_5B fractions are about 120 and 200 mg. resp. in most cases. The data in 99 and 104 seem out of line. For the C_4 anilide the yield is a little more varied, averaging out to 281 mg. The yield of the two C_3 fractions seems to be about 100 mg. each.

Accuracy of fractionation. In Table II are given comparisons of the yields of saccharinic acids, calculated from the anilide yields, with those obtained by J. U. Nef [Annalen 376, (1910)]. The agreement seems to be quite good, the total being a little higher than that obtained by Nef. Nef made no attempt to separate his mixture of acids quantitatively, being limited at that time to a technique of fractional crystallization.

TABLE II

COMPARISON OF YIELDS OF SACCHARINIC ACIDS FROM XYLOSE WITH THOSE REPORTED BY NEF

Process	Mg. Yields, based on 1 gram xylose				
	C_3	C_4	C_5A	C_5B	Total
Cellulose Column	57	165	81	128	430
Reported by Nef	----266----		----154----		420
Reported by Nef for arabinose	----216----		----267----		483
Reported by Nef for glucose	400-450	100-150	----------		600-700

This author still feels that the yield of lactic acid (C_3) obtained in this project is low. It will be noted earlier in this report that only 26.0 grams of sirupy anilides were obtained from 25.6 grams of sirupy acids. If it is assumed that these acids were all C_5 acids, the yield of anilides should be 38 grams, whereas if they were all C_3 acids the yield would be 46 grams. The actual yield, instead of being between these two values is below the lower one.

Nef did more detailed analyses on the acids from glucose, and obtained a 40-45% yield of the C_3 acid here. It may be that the C_5 sugars do not give high yields of this acid, not being able to split into two C_3 fragments, as can a C_6 sugar.

The nine fractionations given in Table I were all made from aliquots of one sample, or from one conversion of saccharinic acids to the anilides. Hence they show only the accuracy of the fractionation, and not the precision of anilide conversion. Perhaps in future work on black liquor an attempt to test completeness of anilide formation should be made, by heating with water-entrainers, as benzene or toluene for varying lengths of time. This has been done in the preparation of lactic anilide by Fein and Filachione [J. Am. Chem. Soc. 75, 2007 (1953)]; an 87% yield was reported.

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ALKALINE PULPING OF JACK PINE AND COTTON LINTERS

This work deals with the alkaline pulping of a sample of jack pine and of cotton, in an effort to study saccharinic acids as possible "end-groups" on the resulting pulps. Samuelson and Wennerblom (1) originally noted the increase in carboxyl groups with extended alkaline pulping, an effect not influenced by the presence of oxygen (2). Machell and Richards (3) have shown that glucometasaccharinic acids are present as end-groups on alkali-treated hydrocelluloses.

Yields of crude wood-pulp resulting from normal kraft and soda cooks of jack pine were comparable (43 and 42% respectively) but that from a kraft "over-cook" was much less (30%). Consumption of alkali during the over-cook was much greater than that of the normal cook.

Samples of black liquor were acidified, and the precipitated lignin isolated, after washing by a freezing-thawing technique (4). Yields of lignin were greater for the normal kraft cook than for the over-cook. The yield of organic solids in the acidified filtrates was less for the normal cook (15.1%) than for the over-cook (21%). The total of nonvolatile material recovered from the various black liquors ranged from 62 to 76% of the total wood dissolved during the cooking action.

The yields of linters resulting from a normal kraft cook of cotton linters was 88%, and that from an overcook only 44%. The yield of nonvolatile solids (all saccharinic acids?) in the black liquors were 83 and 70% resp. of the total materials dissolved. The balance is probably formic acid.

Experimental Work

Cooking conditions. The wood used in the several cooks was jack pine, obtained from the Thilmany Pulp and Paper Mill at Kaukauna. Three sticks were peeled and a 1-foot section of each converted to sawdust. The remainder of the three sticks was chipped to a nominal 3/4 inch size, screened and hand-sorted for knots and slivers.

The cotton used was "Acetate Grade Linters Pulp, Type 1-Ay-500", supplied by The Buckeye Cellulose Corporation.

The cooking conditions are given in Table I and II, as carried out by the Pulping Group; stationary digesters 2 and 4 were used (5). In each case about 20 liters of strong black liquor were collected, and about 20 liters of washings. The latter were obtained by washing the pulps in a centrifuge. Undoubtedly a small amount of liquor was not removed in this limited washing, and was lost later in screening.

Concentration of these liquors, with a pH of 13.5-14, was accompanied by foaming. So they were partially neutralized with 6 normal sulfuric acid. The black liquors from the cotton cooks were neutralized to pH 9. The pH of black liquors from the wood cooks were reduced to 12 only, as below this value lignin began to precipitate. In all cases the liquors were concentrated in vacuo at a temperature of 50-60° to a volume of 8-10 liters.

Table I

Alkaline Pulping of Jack Pine

	Cook 1	Cook 2	Cook 5
Type of cook	kraft	soda	kraft
Grams wood, o.d. basis	4093	4093	4093
Water used, liters	25.3	25.3	25.3
Water-wood ratio, cc./g.	6.2	6.2	6.2
Wt. of wet wood	8183	8175	8141
Active alkali, as Na_2O, % of wood	24.16	24.16	24.16
Calcd. Na_2O, in grams	989	989	989
Sulfidity, % of Na_2O	25.7	---	25.7
Wt. NaOH, as grams Na_2O	735	989	735
Wt. Na_2S, as grams Na_2O	254	---	259
Maximum temp., °C.	172	172	172
Time up to temperature, hrs.	1.5	1.5	1.5
Time at temperature, hours	1.5	3.0	20
$KMnO_4$ number of pulp	17.7	22.7	---
Unscreened pulp, % yield	42.83	41.93	30.49
Screened pulp, % yield	41.17	38.70	30.44
Screenings, % of total yield	3.88	7.69	0.16
Screened pulp, grams	1753	1716	1209

Table II

Alkaline Pulping of Cotton Linters

	Cook 3	Cook 4
Type of cook	kraft	kraft
Grams cottons, o.d. basis	1296	1296
Water used, liters	25.46	25.46
Water-cotton ratio, cc./g.	19.5	19.5
Weight of wet cotton, grams	1364	1364
Active alkali, % of cotton	76.3	76.3
Calcd. Na_2O, in grams	989	989
Sulfidity, % of Na_2O	25.7	25.7
Wt. NaOH, as grams Na_2O	735	735
Wt. Na_2S, as grams Na_2O	259	259
Maximum temp., °C.	172	172
Time up to temperature, hrs.	1.5	1.5
Time at temperature, hrs.	1.5	20
Screened cotton, % yield	88.27	44.0
Screenings, % of total yield	0	0
Screened cotton, grams	1144	570

It was felt that the black liquors would be more stable during long-time storage if the pH was lowered. A slight alkaline oxidation does occur, as a slight vacuum is noted when any stoppered bottles are opened for sampling.

Analysis of liquors. The black liquors derived from cotton were neutralized by passing 500-ml. portions through a cation-exchange resin (LI-120) to replace sodium ion with hydrogen ion. Some gas was evolved. The cloudy effluent was cleared by filtration through Celite filter-aid. This cloudiness, apparently a precipitate of sulfur, reappeared within 24 hours, so the best procedure is to let the solution stand for several days, and then filter.

The acidic solutions were then neutralized with barium carbonate to pH 4. The filtered solutions gave no further precipitate with barium acetate, thus showing complete removal of sulfate ion. The sulfate-free solutions were then run through a cation-exchange resin again to give a barium-free effluent with a minimum pH of 2.2. The column was washed until a pH of 3.8 was reached. The solution and washings (about 13 liters) in each case was concentrated to a sirup and the latter dissolved in ethanol. Aliquots were concentrated in weighing bottles and dried *in vacuo* at 60° to determine the total weight of nonvolatile solid. The final product was a dark red viscous sirup, presumably all saccharinic acids. Yields are given in Table III.

Table III

Analysis of Black Liquors from Cotton Kraft Cooks

	Cook 3	Cook 4
Cotton dissolved, %	56	69.5
Cotton dissolved, grams	152	726
Acid needed to neutralize total liquor to pH 9, in meq.	25,200	19,900
Acid-soluble nonvolatile material, in grams	126	504
Recovery of cotton dissolved, as black liquor constituent, %	83	69

Black liquors derived from wood (500 ml. portions) were added to an excess (220 ml.) of 6 normal sulfuric acid with stirring. The mixture, after standing overnight, was filtered to give a solution of pH 1.9. The insoluble lignin was stirred with 1500 ml. of water, the slurry poured into two 1-liter polyethylene bottles and allowed to freeze overnight in a refrigerator. They were then thawed out and the resulting mixture easily filtered. This type of washing (4) was repeated 4 times until a pH of 3.5 was obtained.

The aqueous solution (about 9 liters) was neutralized with barium carbonate and worked up as were the black liquors derived from cotton. The lignin precipitate was air-dried and weighed. Data are given in Table IV.

Future Work

The two cotton pulps will be hydrolyzed and the acidic portion separated from the bulk of the glucose. This will be done with a basic De-Acidite resin buffered with ammonium carbonate. The absorbed acid fraction will be converted to the anilide and fractionated. Presumably it will be a mixture of glucometasaccharinic acids.

Attempts will also be made to isolate such saccharinic acids from the wood pulps. This will be more difficult, as uronic acids will be present.

Table IV

Analysis of Black Liquors from Jack Pine

	Cook 1	Cook 2	Cook 5
Type of cook	kraft	soda	kraft
Wood dissolved, %	57.3	58.1	69.5
Wood dissolved, grams	2340	2377	2884
Acid needed to neutralize total liquor to pH 12, in meq.	9600	12,600	3800
Weight of acid-insoluble lignin	1132	986	906
Yield, based on wood, %	27.6	24	22
Weight of acid-soluble nonvolatile material	620	666	890
Yield, % based on wood	15.1	16.2	21
Total yield of liquor constitutents	42.7	40.2	43
Recovery of wood dissolved, as liquor constituents	76	70	62.5

The mixtures of saccharinic acids present in the several black liquors will be converted to the anilides and fractionated by paper chromatography. Attempts will be made to correlate the yields with the carbohydrates dissolved from the wood during the pulping process. Samples of the several black liquors will also be acidified and the volatile components isolated

Fractionation of saccharinic anilides in the past (see Report Seven) has been carried out with the aid of acetone and petroleum ether. In observance of a revised safety code, less flammable solvents (methyl isobutyl ketone and n-butyl ether) are being investigated.

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4. F. J. Ball (to West Virginia Pulp and Paper Co.) U. S. 2,813,090, Nov. 12, 1957. C. A.

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ALKALINE PULPING OF JACK PINE AND COTTON LINTERS

This report is a discussion of some analytical data obtained on several alkaline pulps. Details of the cooking conditions are given in Report No. 8. The analytical work was done by the Analytical Group and is given in Institute File No. 180530/535.

The alkaline cooking conditions remove the araban and galactan very rapidly, and most of the mannan in the wood. The xylan is removed more slowly. There is a greater removal of glucan by the soda cook than by the kraft cook. A normal kraft cook removes more glucan from wood than from cotton, but in a longer kraft cook the reverse effect holds. With increasing cooking time the viscosity of both wood and cotton pulps drops; the carboxyl content decreases for the wood pulps but increases for the cotton pulps.

DISCUSSION

The data are summarized in Tables I and II. The kraft and soda pulps analyzed were unbleached. The analyses for the soda and 3-hour kraft wood pulps are similar. The lower yield of soda pulp seems to be attributed to a greater loss in glucan content. Thus, 24% of the glucan

TABLE I

ANALYSIS OF ALKALINE PULPS

		Wood Pulps			Cotton Pulps	
	Wood	3-Hour kraft	3-Hour soda	20-Hour kraft	3-Hour kraft	20-Hour kraft
Yield, %		41.2	38.7	30.4	88	44
Glucan, %	38.5	80.0	75.6	84.1	91.84	92.77
Mannan, %	9.97	5.65	5.71	4.44	---	---
Xylan, %	6.30	6.77	5.45	4.83	---	---
Araban, %	1.66	0.66	0.58	0	---	---
Galactan, %	3.34	0.64	0.68	0	---	---
Carboxyl, %	0.39	0.29	0.29	0.18	0.05	0.21
Copper-ethylene-diamine, viscosity, centipoises	---	19.7	10.8	3.49	4.09	1.92

Note - the glucan content of the original cotton was 95.8%.

TABLE II

REMOVAL OF POLYSACCHARIDES DURING PULPING

	Individual Polysaccharides, %				
	Glucan	Mannan	Xylan	Araban	Galactan
Polysaccharides in original wood	38.5	9.97	6.30	1.66	3.34
3-hour kraft cook					
Content in pulp	80.0	5.65	6.77	0.66	0.64
Content, based on wood	32.8	2.33	2.79	0.27	0.26
Loss, based on wood	5.7	7.64	3.51	1.39	3.08
Loss, based on total polysaccharide	15	77	56	84	92
20-hour kraft cook					
Content in pulp	84.1	1.44	4.83	0	0
Content, based on wood	25.5	1.35	1.47	0	0
Loss, based on wood	13.0	8.62	4.83	1.66	3.34
Loss, based on total polysaccharide	34	87	77	100	100
3-hour soda cook					
Content, in pulp	75.6	5.71	5.45	0.58	0.68
Content, based on wood	29.2	2.21	2.11	0.22	0.26
Loss, based on wood	9.3	7.76	4.19	1.44	3.08
Loss, based on total polysaccharide	24	78	66	87	92
Polysaccharides in original cotton	95.8				
3-hour kraft cook of cotton					
Content in pulp	91.84				
Content, based on cotton	80.5				
Loss, based on cotton	15.3				
Loss, based on total glucan	16				
20-hour kraft cook of cotton					
Content in pulp	93				
Content, based on cotton	41				
Loss, based on cotton	54.8				
Loss, based on total glucan	51				

is removed by the soda cook, and only 15% by the kraft cook. The longer kraft cook removes 34% of the glucan, a considerable loss.

The araban and galactan are very readily removed from the wood by either process, and the longer kraft cook removes these two polysaccharides completely.

The mannan is removed almost as readily in the shorter cooks as are the araban and galactan. However, longer cooking time does not remove much more of the mannan, the loss increasing from 77 to 87%. Thus, 13% of the original mannan in the wood seems to be resistant to the kraft process.

Xylan is even more resistant than mannan, and after the longer kraft cook 23% of the original xylan is still in the pulp. The soda cook removes a little more xylan in a 3-hour period than does the kraft cook.

No analysis was made for polyuronides, but the carboxyl content of the wood pulps decreases with longer cooking time, showing removal of this constituent. However, it will be noted that for the two cotton pulps the carboxyl content increases with cooking time; this is attributed to isomerization of reducing end groups to saccharinic acid units. The decrease in carboxyl content of the wood pulps may be a combination of a decrease in uronic acid units and an increase in saccharinic acid units. Thus the removal of polyuronide material may be greater than shown by the carboxyl content.

In the case of cotton, the loss of glucan (16%) in a 3-hour kraft cook is very close to that for the loss of glucan (15%) for a similar cook with wood. For the longer kraft cooks, however, the loss of glucan is much greater for the cotton (51%) than for the wood (34%). This may be attributed to the greater amount of active alkali used in the cotton cooks; 76% active alkali was used for the cotton, and only 24% for the wood. Cann and Roberson (1) have noted this effect of active alkali on the yield for pulping of southern pine. In this work the concentration of alkali was kept the same for cooking of cotton and wood; the wood-water and cotton-water ratios were different, however, because of the bulkiness of the cotton.

The viscosity of the wood pulps showed a decrease for longer cooking times, and also a greater decrease for the soda cook over the kraft cook. It would be interesting to run a soda cook on cotton to see if a similar effect would be observed.

Calculations from the carboxyl content of the two cotton pulps, with the assumption that this carboxyl content is caused by a C-6 saccharinic acid end unit (2), give values of 516 and 123 for the chain lengths of these two pulps. Nitrate viscosities should be run to confirm these magnitudes of D.P.

Future work will include the hydrolysis of these two cotton pulps to give mixtures of glucose and a small amount of saccharinic acid. Fractionation on a buffered basic ion-exchange column (2) should allow separation of the acid and its identification. This has been done by

Machell and Richards for an alkaline-treated hydrocellulose, but not for a cotton of high D.P. or a wood pulp under pulping conditions. Hydrolysis of the wood pulps and similar fractionation might give a mixture of uronic acids and saccharinic acids. One or more of the saccharinic acids might be of the C-5 type, derived from xylan. Any acids derived from mannan could not be distinguished from those arising from glucan, as the C-2 hydroxyl is isomerized in saccharinic acid formation.

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Use of a Scintillation Counter with Aqueous Solutions of Carbohydrates

Recently the Biology Department has acquired a Beckman liquid scintillation counter; this employs a "cocktail mixture" composed of dioxane, napthalene and a certain amount of a scintillation agent ("PPO or POPOP"). With a printout device and an endless track to take 100 samples, the instrument can be cperated automatically with very little attention from the operator.

Since the dioxane solution contains about 10% naphthalene, this system is not a good solvent for water-soluble carbohydrates. The latter can be added as an aqueous solution to the system, up to 20%. There is a quenching action by the water, giving a reduced count for the substrate. This effect, however, seems to be linear, and the attached graph shows this effect. In the range studied, from 300 to 1500 mg. of water added per 20 ml. of cocktail, or 1.5 to 7.5% water, the reduction in count is about 2.5%. So it is best, for work on relative counts, to always use the same amount of water to standardize this quenching factor.

Experimental

A solution of methyl-β-D-glucopyranoside, with a radioactive label (C-14) on the methyl group, was made up in water and measured out in a weight buret. The concentration of glucoside was 12.8 mg./gram solution.

Six solutions were made up, with varying amounts of solution and water, and added to the cocktail solution (about 20 ml.). The data are given in Table I, and the plot of the counts obtained Figure 1. The counts are given as counts/minute/milligram and represent the average of 8 measurements for each solution.

TABLE I

Count Obtained for Glucoside with Varying Amounts of Water

Solution, mg. added	Water, mg. added	Total water, mg. added	Glucoside, mg. added	Count per min.	Count/min./mg.
302	none	298	3.86	25571	6625
304	401	701	3.885	25479	6558
293	741	1030	3.745	24438	6526
601	none	593	7.68	50501	6576
606	389	987	7.74	50451	6518
627	743	1362	8.02	51586	6465

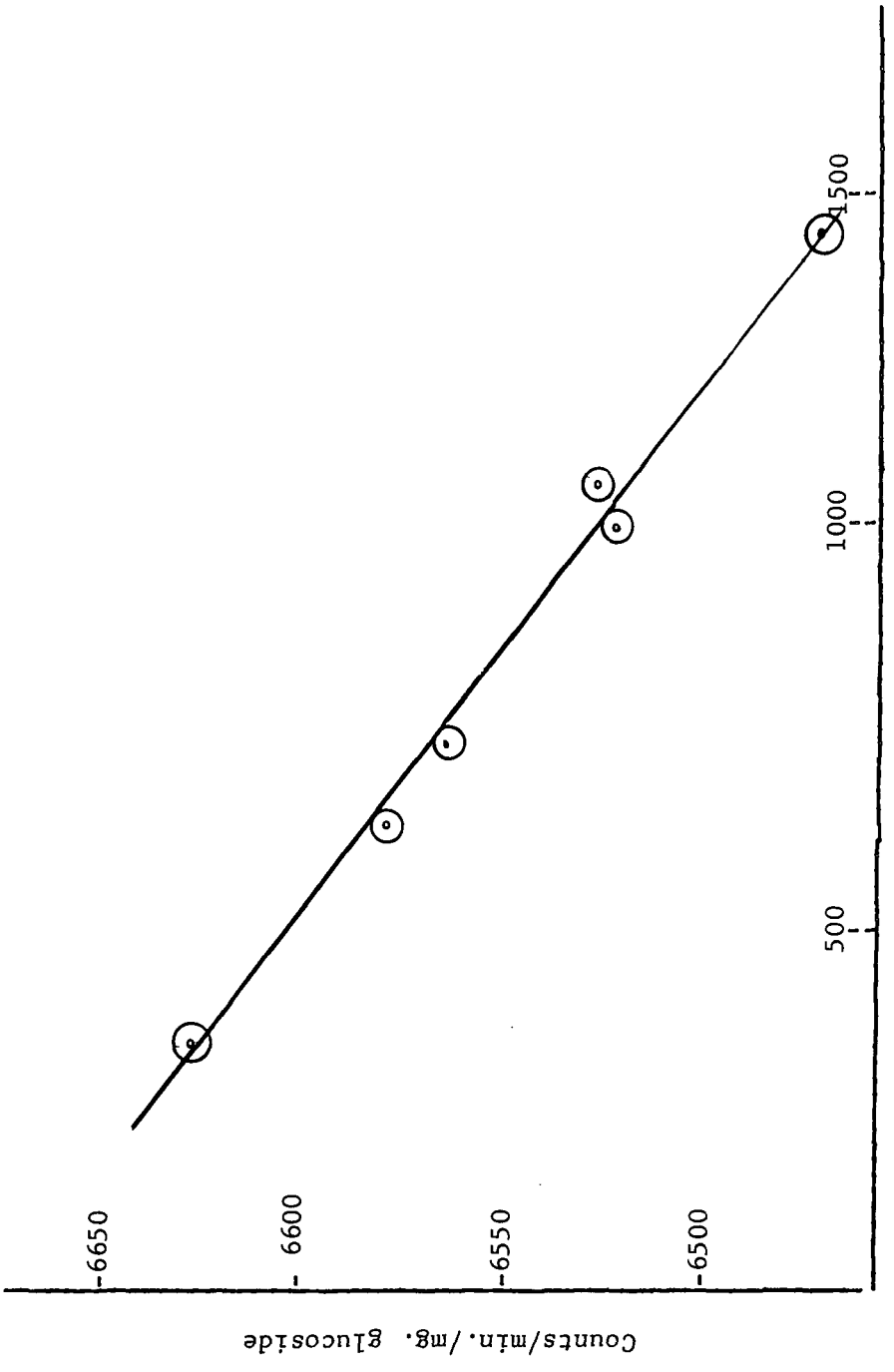

Figure 1. Quenching effect of water added to "ocktail" solution.

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GAS CHROMATOGRAPHY OF SACCHARINIC ACIDS

Several preliminary experiments were tried on the analysis of mixtures of saccharinic acids, as derived from treating sugars with alkali, or from kraft black liquor. The trimethylsilyl derivatives were run on the gas chromatograph; these TMS derivatives were derived from (a) the lactones, (b) the acids, (c) from the anilides. It was concluded that the TMS derivatives of the acids were best, in that only one major peak was obtained for a given acid, and very small minor peaks were observed for lactones present. Attempts to convert a mixture of acids and lactones, present in a reaction mixture, to the lactone only was unsuccessful, and several peaks were obtained. Attempts to convert a lactone completely to the anilide were unsuccessful also.

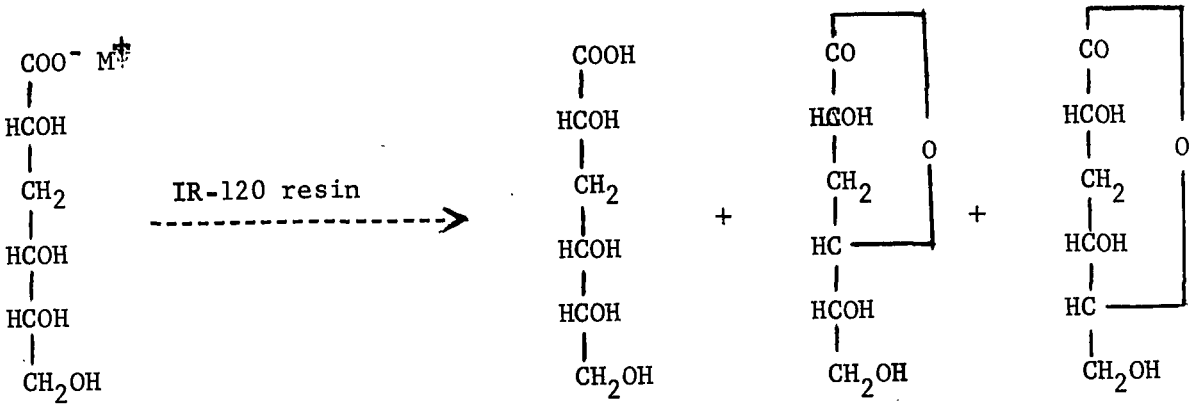
Discussion of Experimental Results

Saccharinic acids exist in alkaline solution only as the straight chain anions (I), but in acidic solution, after removal of the cation with a cation-exchange resin, a mixture of the free acid (II) and one or more lactones (III and IV) is formed. Depending on the given saccharinic acid, the ratio of free acid to lactones will vary; some acids may exist almost entirely as a lactone, while others may have a high proportion of the straight chain acid. In some earlier work done at the Institute (1), it was found that the mixture of saccharinic acids derived from a kraft black liquor was composed of 2/3 lactones and 1/3 acid. This analysis was based on the fast titration

of the free acids with alkali, whereas the lactones react more slowly and a second titration is therefore carried out at a higher temperature.

Ishizu, Lindberg and Theander (2) have recently reported on the quantitative gas chromatography of the lactones of saccharinic acids, run as the TMS derivatives on a butanediol succinate column at 160°C. Alkaline reaction mixtures, derived from treating various sugars with sodium or calcium hydroxide, were first treated with a cation-exchange resin, and the acidic solution concentrated. This "concentrated solution was given a brief treatment with Dowex 3 (free base) in order to remove free acids and concentrated." The lactones remaining in solution were then analyzed as the TMS derivatives. No attempt was made to determine the free acids taken up by the Dowex resin, and therefore the quantitative analysis reported by these authors is on a lactone basis only.

Attempts to use the technique of Ishizu et al. (2) were unsuccessful in that several peaks were obtained for a single saccharinic acid. This was expected, that at least two peaks would be obtained, one for a lactone and one for the free acid. Thus a solution of calcium α-glucometasaccharinate, after being deionized with Amberlite IR-120 resin, concentration to dryness, and conversion to the TMS derivative, gave two peaks, a fast one for the lactone and a slow one for the free acid. The areas of these peaks were about the same. A solution of calcium β-metasaccharinate also gave two peaks, but the area of the free acid peak was much greater than that of the lactone peak. In contrast sodium isosaccharinate gave a large lactone peak, corresponding to the known 1,4-lactone, and also another small peak which may be the unknown 1,5-lactone; a very small peak was present, representing the free acid. Hence



I II III IV

the ratio of lactone to free acid in an aqueous solution varies according to the particular saccharinic acid.

The more successful approach has been to treat a sodium or calcium salt directly with the Tri-Sil reagent; this has given in several cases a very large peak for the free acid and only very small peaks for the lactones. This means that a quantitative evaluation of a given peak should represent most of the given saccharinic acid. Thus calcium β-glucometasacchrinate gave only one peak, of retention time of 15.9 minutes, and no peak in the faster lactone region. Similar results were obtained with potassium arabinonate; this compound is not a saccharinic acid but of similar behavior. The potassium salt gave a large free acid peak at 11.2 minutes, and only two very small peaks (less than 1%) at 4.9 and 6.3 minutes; the deionized solution gave much larger lactone peaks.

Attempts to convert a saccharinic acid lactone completely to the anilide by heating the lactone with aniline and acetic acid in ethanol was unsuccessful; the resulting product contained about equal parts of lactone and anilide. This approach was tried because much previous work with paper and cellulose column chromatography of saccharinic acids was (3) done with this type of derivative and crystalline samples of various compounds were available. It may be possible to convert these anilides to sodium salts by heating with alkali, and then react these salts to obtain the TMS derivatives of the free acids.

In summary it seems best to confine future work to the TMS derivatives of the free acids (the free acid or FA method) derived from the salts, rather than to work with lactone-acid mixtures (the lactone-acid or LA method) obtained

by deionizing aqueous solutions of salts and then concentrating the acidic solutions. The free acid samples will run more slowly, have longer retention times, than will the lactones in the lactone-acid mixtures, but the pattern will be less complicated, with only one peak per given saccharinic acid. The LA method may give "duplicate" peaks for a given saccharinic acid, representing the lactone and the free acid. In some cases the mixture may be mostly lactone, as mentioned earlier for isosaccharinic acid.

Several analyses were run on mixtures of saccharinic acids obtained by treating glucose with hot 8N sodium hydroxide. A series of peaks was obtained, most of which have yet to be identified, i.e., compared by retention time with known samples. The dominant peak, for the LA method, was at 9.3 minutes, which is probably the C-6 glucometasaccharinic lactone. At least seven other peaks were obtained, ranging from 1.2 to 6.6 minutes. When the system was analyzed by the FA method, the dominant peak moved to 16.2 minutes. Five other peaks were obtained, ranging from 1.8 to 10.8 minutes. Shifting from the LA method to the FA method increased the retention times but also decreased the number of peaks, i.e., may have eliminated duplicate peaks. This glucose mixturesshould consist of at least two C-6 meta acids, two C-5 meta acids, one C-4 and one C-3 acid.

An arabinose system, similarly treated with hot 8 N sodium hydroxide, gave, by the LA method, at 160° column temperature, six peaks. The two slowest ones presumably are the two C-5 meta lactones or acids. Programming from 130° to 160°, at 2° per minute, gave twelve distinct peaks. This system was not run by the LA method, which might reduce this large number of peaks.

Preparation of the TMS derivatives of free acids. (FA method)

A sample of potassium arabinonate was treated with Tri-Sil and a single peak obtained with a retention time of 11.2 minutes; this compares with 11.4 minutes found earlier for a mixture of acid and lactones. Also two very small peaks (less than 1%) were found at 5.0 and 6.3 minutes (4.9 and 5.7 minutes noted earlier).

As mentioned earlier, the calcium salt of β-glucometasaccharinic acid was treated directly with Tri-Sil and a single peak obtained at 15.9 minutes.

It is assumed that in the reaction with Tri-Sil initially the reagent (Me_3SiCl) reacts with a hydroxyl group (active hydrogen) to give the ether and liberate HCl. This HCl apparently reacts more rapidly with the cation of the saccharinate salt (RCOOM) than with the pyridine to form the free acid and the chloride salt. The free acid will then react, via the carboxyl group, to form

$$Me_3SiCl + ROH \longrightarrow ROSiMe_3 + HCl$$

$$RCOOM + HCl \longrightarrow RCOOH + MCl \longrightarrow RCOOSiMe_3$$

the silyl derivative. As the hydroxyl groups on the carbon chain are blocked very rapidly by silyl groups, there will be little opportunity for the carboxyl group to react with one of these to form either the 1,4- or the 1,5-lactone.

A deionized reaction mixture, resulting from the treatment of glucose with hot 8 N sodium hydroxide, had a pH of 3.5. This was titrated with N sodium hydroxide at 70° to a pH of 9.8. At this pH presumably all the lactones as well as the free acids were converted to the sodium salts. This solution was then concentrated to dryness (a 2-ml. aliquot) and the residue treated with Tri-Sil reagent. By this FA method the peaks obtained were of greater retention time than obtained by the LA method.

Preparation of TMS derivatives of lactone-acid mixtures. (LA Method)

Five mg. of a known lactone (α-isosaccharin or α-D-glucosaccharin) was treated with 0.5 ml. of a Tri-Sil reagent in a dry vial; the mixture was shaken, and after 5 minutes a 2 microliter portion injected into the gas chromatograph. In both cases a single peak was obtained.

In the case of α-glucometasaccharin, 5 mg. of the calcium salt dissolved in 1 ml. water was treated with IR-120 cation exchange resin and the resin washed with 10 ml. water. The solution was concentrated to dryness, some absolute ethanol added and the solution reconcentrated. The residue was treated with 1.5 milliliters of Tri-Sil reagent and then 2 microliters injected into the gas chromatograph. Two main peaks were obtained, one at 9.3 minutes, the other at 17.1 minutes. The relative areas of these peaks were 83 and 98. In the case of the Ca β-metasaccharinate, again two peaks were obtained, of the same retention times as before, but the relative areas were 45 and 130. It was assumed that the faster peak was the lactone, the slower one the acid. (This was confirmed by treating the Ca β-metasaccharinate with Tri-Sil; only the slower minute peak was obtained.) Attempts to convert the acid in these mixtures to the lactone by refluxing with ethanol was without effect.

A similar mixture was obtained in the case of potassium arabinonate. The salt was deionized with IR-120 as above; the TMS derivative gave one large peak at 11.4 minutes, and two smaller peaks at 4.9 and 5.7 minutes. Attempts to lactonize by heating with ethanol reduced the large peak, increasing the two smaller peaks, but also a new peak was formed at 9.9 minutes, presumably the ethyl ester.

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Effect of Alkaline Dimethyl Sulfoxide on Cellulose

About four years ago Ward et al. (1) published a paper on the carboxymethylation of cotton linters. The reaction was carried out in two steps (a) steeping the linters in a solution of chloracetic acid for 30 minutes, then filtering off the liquid and pressing the fibers dry; (b) steeping the fibers for a short period (generally 1 hour) in a sodium hydroxide solution. The alkaline solution was then removed and the fibers soaked in aqueous acetic acid and finally converted in aqueous sodium bicarbonate to the sodium salt. Three solvents were used for the chloracetic acid and sodium hydroxide solutions; they were water, iso-propanol, and dimethyl sulfoxide.

The interesting thing about this work was that in a series of experiments where the only variable was the concentration of sodium hydroxide, the viscosity of the product decreased as the concentration of alkali increased. These experiments were not run too closely as to time, concentration or temperature; the main interest was in the D. S. of the product and the physical properties of the resulting handsheets. However the data for DMSO given in Table I can be plotted, log of viscosity versus concentration of sodium hydroxide, and a roughly linear plot is obtained. (Figure 1). This would infer that either (a) the sodium hydroxide, as a very active base in an aprotic solvent, is degrading the cellulose, or (b) the dimethyl sulfoxide is oxidizing the cellulose and this oxidative action is proportional to the alkali concentration. DMSO is known to be an active oxidant, but generally only in the presence of dehydrating agents, such as acetic anhydride or phosphorus pentaoxide.

That the DMSO is a definite factor in the degradation can be seen by comparing the data given in Table II for the three solvent systems at 70-80°; far more degradation (lower viscosities) is obtained for the DMSO system, and at lower sodium hydroxide concentrations. Iso-propanol has an intermediate position and very little degradation occurs in water.

The viscosity data of course are of the carboxymethyl derivatives, and not of unsubstituted cellulose, and therefore cannot be interpreted too closely. But there is a definite trend for the three solvent systems, and also increasing alkali produces more degradation, especially for the DMSO system at low akali concentrations.

It has been thought that the effectiveness of various alkalies in aprotic solvents, such as dimethyl sulfoxide or dimethylformamide, is due to the lessened solvation of the base. In contrast an aqueous solution of sodium hydroxide is surrounded by a large solvent cage and this cage interferes with the reaction of the base with any substrate in solution. Thus sodium benzoate in DMF has been found to be quite an effective base, in contrast to the ineffectiveness of the aqueous solution.

A more critical set of experiments, to determine the effect of alkaline solutions in dimethyl sulfoxide, without the preliminary treatment with chloracetic acid, would be of value in studying the alkaline degradation of cellulose.

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Table I

Comparison of Solvent Effects at Room Temperature

Solvent	Concn. of NaOH %	Reaction Time hours	Viscosity of Product centipoises
DMSO	0	1	37.7
	0.3	1	33
	0.3	1	30
	0.3	1	31
	0.3	1	32
	0.4	1	27
	1.0	1	19.4
	1.2	1	18.1
	1.2	18	7.0
Iso-propanol	0	1	37.7
	0.3	1	39
	0.3	1	32
	3.6	0.5	30
Water	40	0.2	11.5

Table II

Comparison of Solvent Effects at 70-80°C

Solvent	Concn. of NaOH %	Reaction Time hours	Viscosity of Product centipoises
DMSO	0.3	1	10.7
Iso-propanol	1.0	1	22.3
Water	10	1.5	31
	20	1.5	24

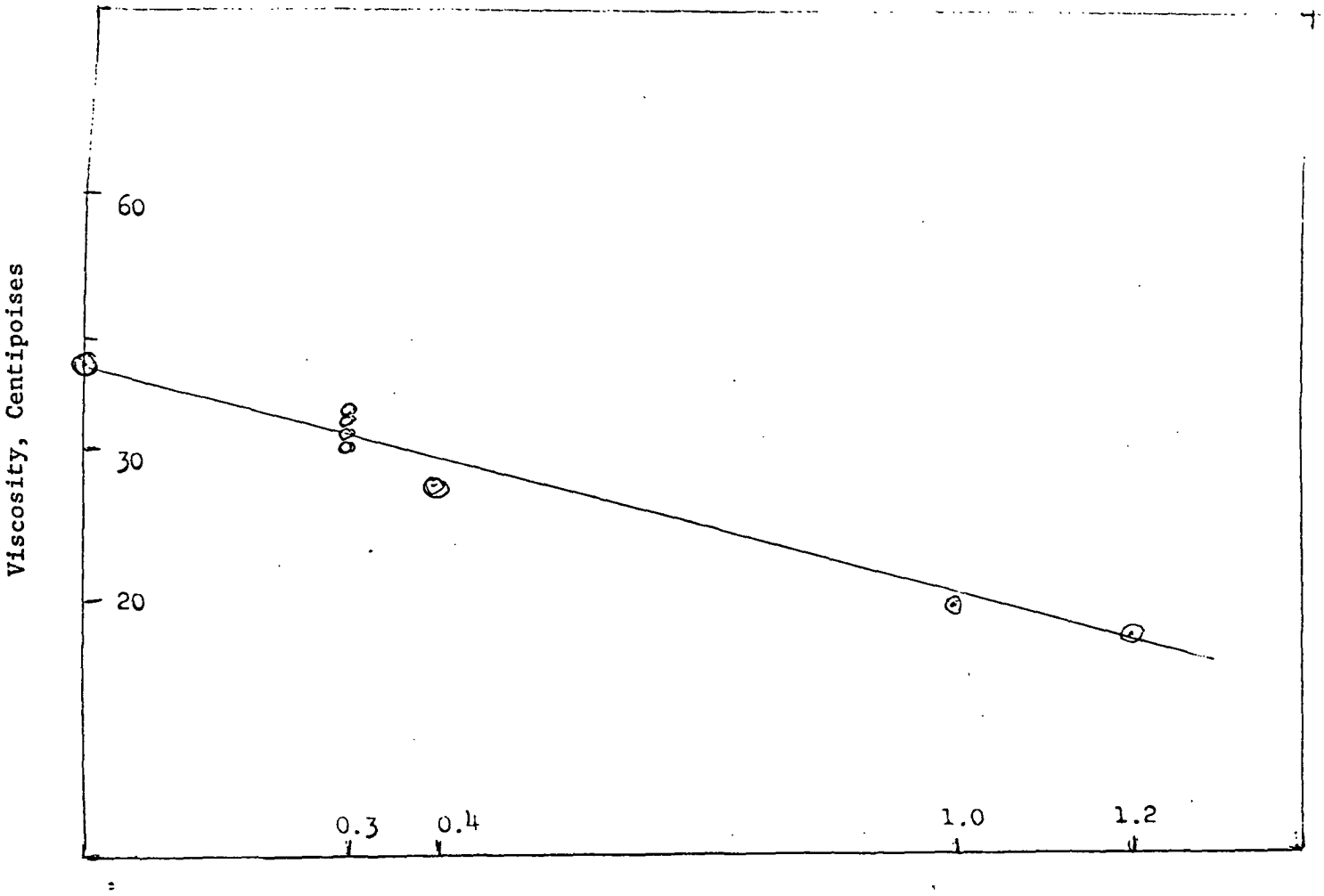

Figure 1 - Effect of Alkali Concentration on Viscosity