

mixture of 40 gms d. galactose, m.p. 155-70, 400 gms H₂O and 20 gms ^{3 eq +} fused CaO (Ca 7K) was allowed to stand O.T. covered, partially, shaking t. lot. for 55 days; the mass at first almost gelatinous but afterwards became more mobile. It was filtered off & ppt washed well (in cold). Wet ppt dried in vac H₂O was 31.8 gms; it contained 35.09 % CaO as det'd by gravimetry. 1.5649 gms gave 0.1982 gms CaO. The ag. filtrate was sat'd. Ca₂ then let to become filtered off from CaCO₃ in 200 cc = 5.1 gms. The combined ppts were now dissolved in H₂O containing 22 gms CH₃COOH and then the Ca ppt'd by the amt. of hot CrO₄ H₂SO₄ = 31.2 gms) solution. The ag. filtrate dist'd at 25 mm left a faint brown gum: this was dissolved in H₂O and treated with 10 gms pure CaCO₃; fol. 7.1 gms insol. salt after digestion & this left on treatment with dil. acetic 2.1 gms insol. CaCrO₄. The ag. filtrate was digested with K₂CO₃ and on concn to small volume no Ca salt sep. out: added finally alcohol etc. & neither got a separation of ^{24 gms} ~~Ca d. the same~~ ^{supernatant} ~~filtrate~~ ^{see below.}

7r II 22.4932 grs lost after drying 36 hrs 70-90° 1.4968 grs H₂O = 6.68%
 the anhydrous salt is very hygroscopic, dissolves in H₂O with heat evol. & effervescence. (noticed a decided smell of alcohol.)
 dry salt 0.1600 grs CaSO₄ = 11.53% Ca ← ~~theory = 12.97%~~ (present)
 7.36% C₂O₄H₂·2H₂O =

Fr I; analysis 14.0528 gm as dry salt lost after drying 70-75%
anhyd. salt shows same props as Fr II: 0.6035 gm anhyd. salt gave c. H₂SO₄ 0.1999 gms Ca SO₄ = 9.74 = Ca theory = 9.74
anhyd. salt shows same props as Fr II: 0.6035 gm anhyd. salt gave c. H₂SO₄ 0.1999 gms Ca SO₄ = 9.74 = Ca theory = 9.74
anhyd. salt shows same props as Fr II: 0.6035 gm anhyd. salt gave c. H₂SO₄ 0.1999 gms Ca SO₄ = 9.74 = Ca theory = 9.74
anhyd. salt shows same props as Fr II: 0.6035 gm anhyd. salt gave c. H₂SO₄ 0.1999 gms Ca SO₄ = 9.74 = Ca theory = 9.74

The University of Chicago

This was dissolved in boiling water and dyed with 24.7 grs Buem; ext to sol 2x by ethel₃ and evap ag. filler on B.U.B. powder H₂O in new jar & 23.4 grs Br salt; this was dissolved R.F. in 133 cc absd. alcohol and on standing ot for 48 hrs got a separation of ^{an. and} 1/3-5 grs gum which was decanted off and now combined with corresp. lot from Fr II (blue pencil), and dissolved in water group, Buem. for some time; total gum = 11.3 grs; heated in H₂O solution with K₂C group again dry H₂O in vacuo. Ut now is 8.2 grs almost whole gum. powder kept 100°-130° (off for 500 lbs up) this dissolved in 300 cc absd. alcohol & let stand comes out rapidly as an oil; the alcoholic filtrate evap. gave 3 grs xx salt; ant of gummy salt coming out must have been 5.2 grs ^(keep) ? is this Buem. hydrate? or is it a Buem. salt of a new acid? H₂Abmice(?)

saccharine (?) - can't tell. Now took all material from Fr I and II except 5.2 grs gummy diff sol. salt and dissolved it in H₂O and add 5 grs CaO powdered etc, got back 38.1 grs Buem and on fpp ling Ca d. thermic by alc. got 19.3 grs salt dried H₂O vac for 18 hrs. This salt was now treated with 600 cc H₂O 196 and 5 grs m.p. in a s.t. Buem for 12 hrs. Added 200 cc H₂O and then ext 2x by ether group C soda solution then dry c. call₂ in this operation there is enough loss thru sep. of used. For lactone (?) : probably not well today either in this way (use K₂CO₃); this was also noticed in corresp. ext No 47 with d. glucose + Ca₂. The other solution on dist off ether left 5-8 cc oil which was dissolved in alcohol and treated with zinc dust left butyrolactone. In this case after action of zinc dust added much ether filler and distill off oil left at reduced pressure; did not work well! but method for getting butyrolactone from the material

For butyrolactone is treatment with H₂O K₂CO₃ etc see No 47 and No — 490 Ca succinate; took 3 grs trimesic acid Ca₂K up to 8-9° in 50 cc H₂O and heated Buem with 3 grs pure CaCO₃; added about 2 L water and heat. Buem for some time (and then filtered hot - on standing over night got only a very small amt. of Ca succinate; the xx are fine needles entirely different from those of d. and new tartaric acid of Ca and for pure sol. in H₂O. The trimesic acid in H₂O (2 L) was treated with dil acetic acid and then got 3.4 grs Ca succinate; emul. and must have gone into H₂O (2 L) as they call for 5.2 grs salt.

500 β Id propionic and soda; took 2 grs Ca₂K's pin/picric acid and shook with an excess of 10% soda solution and then acidified with dil soda and ext to 3x by ether dry CaCl₂ & got back 16 grs pure acid unchanged; can use this as a method for detecting glyceric acid in trixy butyric etc as latter acid gives Id butyrolactone, neutral to soda.

510 Lactulose + ag K₂CO₃; took 20 grs Lactulose 40 grs K₂CO₃ and 2 L. H₂O (amp to 100°/100° NaOH) and sealed up cork paraffin and let stand ot. for 69 days; and found on working up by addition of 60.6 grs 35% HCl etc. that no d. thermic acid or any other acid was formed soluble in acetone. The sol. gave a very strong test with Feh. sol. before HCl addition and there was much blackening on dist off ag. sol at end thus action of HCl on unchanged? Lactulose & H₂O should be repeated but looks as if K₂CO₃ dilute did not transform sugars to acid sol.

(55) Glycerine and HNO_3 1,2; Took 20 grs levulose next 107-9°C at 7K 80 grs H_2O and 2 g PbO_2
and heated R.F. bath 100-110° for ½ hrs [off Lohy de Bruyn got same phenom as in 54]. Filter from
0.55 grs insol yellowish ppt. and distill off H_2O at 25 mm till vol. of solution is about 25 cc & then
add 20 grs conc. esp. HNO_3 (1.2) (i.e. to make acid used about 1,2). After standing in cool H_2O 14 hrs
the mixture was heated in bath at 40-42° for 24 hrs. HNO_3 etc was then dist off at 18 mm
[bath 45-50 and 52° at end]. Residue contains Pb salt; treated R.F., 3x with acetone leaving
7.1 grs insoluble; latter dissolved^{R.F.} with alcohol left 2.9 grs insol salt probably PbNO_3 type
part sol in alcohol gave a gum which was dissolved in H_2O & treated with CaCO_3 powder
together with the acetone extracts. The insol Ca salts weighed 12.4 grs and consisted chiefly of CaSO_3
and CaSO_4 but also a diff sol. Ca salt (? tartrate) is present.
The aq. filtrates of sol. Ca salts now worked up for Ca by bulyne in usual way spot by ppt 2 x
by alc. polyphosph 2x by K_2C 11.5 grs air dry salt; a (det. of amt Ca present (as CaSO_4) gave
10.31 % (theory 11.56). Took salt left 10.9 grs, and treated it in the solution with 3.54 grs
 $\text{CrO}_4 \text{ H}_2$, 2 H_2O (theory) & then treat aq. filtrate in Brm with 22.4 grs Bismuth (= theory) & then
distill off H_2O at 25 mm (bath 53°). The residue easily dissolved in 50 cc hot absd. alcohol
and came out on standing; concluded that L. theorie is acct. must be present.
(very improbable!)
cf Kelowne Acin 205, 171

(56°) Lactulose and HNO₃ 1.2. Took 40% lactulose, kept 100-175 and a little more.
in 63.5 grs H₂O; acid is 1.2] and heated in bath at 40° for 27½ hrs. Distill off at 18-20 mm [bar
42-66° end] and the porous semisolid residue in d.f. is then dissolved in H₂O + dry HCl BuB
with 20 grs powd. CaCO₃. Got 20.2 grs insol salts which deposited H₂O till acetic left only
2.4 grs insol Ca salt effy CaCO₃ probably as before at 3 hrs on BuB. with ½ H₂O gave no diff sol
Ca salt on cooling. The aq. filtrate worked up by digest 2x with K₂C₂O₄ + 2x ppt by alcohol
29 grs brown air dry 24 hrs Ca salts. A det of Ca in this as CaSO₄ gave 10.22 % Ca
[0.4624 grs gave 0.1607 grs CaSO₄]. Took remainder of salt 28.45 grs and heated in H₂O solution
with 9.16 grs CrO₄H₂ H₂O (heavy) and filter and add 57 grs (heavy) Bismuth chloride (Br)
and then exl 1x effy (got back about 10 grs) and then evap BuB day H₂O (24 hrs). Got 69.8 g Bismuth
salt which dissolved R.F. in 140 cc absol. alcohol but on cooling got most of it deposit as a brown
gum.: add 50 cc more alcohol + dissolve on cooling decant fine gummy Bismuth salt much sep. out.
The insol pt was dissolved in H₂O + dry HCl with K₂C₂O₄ and filtrate treated with 5 grs powd. Cu
(CaF₂) lost back Ca salt, as well as Bismuth. Ca salt was combined with comp. salt obs from Br. salt soln
The portion soluble in alcohol was very small in amt: distill off alcohol on W.B. + dissolve alc.
gummy salt obtained in H₂O swamp on BuB. to det its weight: this found to be 17.2 grs + this
Salt was now treated with H₂O and 1.3 grs powd. CaO to break Ca salt and Bismuth + now combine
Ca salts obtained and ppt them again by alcohol. Got a total of 14.25 grs (air dry 24 hrs);
this was analyzed & worked up for d. arabinate of Ca as follows:
{ 14.3057 grs salt dried 18 hrs at 100° lost total of 1.8773 grs H₂O or 13.12 % Ca
0.4519 grs analysed. gave 0.1924 grs CaSO₄ or 12.52 % Ca
Treated the salt left 11.9765 grs in H₂O sol. with 4.72 grs oxalic acid + H₂O (heavy), swamp. aq. filtrate BuB
to a gum and then heat BuB with 10 grs phenylglycine and 100 cc 50% acetic and 15 cc H₂O for 1 hr,
on cooling got a large amt. of brown insol. sugar to sep. out: dig can.
very impure mostly effy. d. arabinic acid but not certain.

The University of Chicago

57 Formose and HNO₃ 1.2. Took 114.4 gms 35% Formalin (ca 7K) : 40 gms CH₂O and 98.5 gms

H₂O and 4.2 gms P₂O₅ (13) and heat 100-105° for 3 hrs (14) then distill off H₂O in bath 60° at 25 mm and add a solution of 57.5 gms HNO₃ 1.42 and 63.5 gms H₂O [i.e. 8 gms 1.2 of 56]. Heat in bath 42° for 24 hrs then distill off HNO₃ in bath 60° at 20 mm. Add H₂O filter from sm. and wash P₂O₅ and deposit with 30 gms powdered CaCO₃. got 23 gr (?) of dry insol Ca salt to wash on deposit. did acetic precipitate all dissolved: no Ca oxalate present. Now sat. filtrate with H₂O to get rid of P₂O₅ present and then evaporate and work up for Ca tetroxy butyrate as usual ppt 2x by decol. got 9.6 gms air salt 24 hrs; this in analysis (C₂H₄O₄) gave 9.54 % Ca 0.4363 gms gave 2.1415 gms CaSO₄. Took rest of salt 9.1197 gms and let stand in vials for 2 days loss of H₂O was 0.9469 gms and on drying 6 hrs more at 90-100° total loss of H₂O was 1.1483 gms or about +12.7% this explains low % of Ca fnd. in xx salt: Dry salt left 8 gms was now treated with 26 cc H₂O 1.96 and 28 red P. in 50 cc Bu₂B for 12 hrs. On adding 75 cc H₂O got a fair amt of insol heavy oil but it is in part very thick : discarded at this point.

58 Glucose and acetic anhydride; thought for some time that glucose, galactose, and formose might be tetroses but finally came to conclusion they are 3x to hexoses mainly. Took 20 gms Saccharose 80 gms H₂O and 2 gms P₂O₅ and concentrated into glucose by heating 1 hr N.F. in bath at 100-110°. Next day heated at 25 mm (bath 70° end) to drive off H₂O add once acetic anhydride to dark brown residue on warming on W.B. some all dissolves, heated bath 100-120° for 6 hrs then distilled off at 25 mm bath 100° end and got 60 cc distillate. Residue in d.f. now weighed 40.5 gms vis pmt entirely soluble in cold ether except sm. amt gum & p₂ salt. Distill off ether solution filter and take 1/4 for fact in vials. got 3.3 gms ppt about 220° at 22 mm with some tar in d.f. then for took rest 3/4 and combine distillates 13 + 3.3 gms and redistill: got 3.9 gms low boiling material acetic acid or anhydride (sol. in H₂O and not but with some tar formation. Heat 200°-220° at 22 mm = 11.1 gms! Body is insol. in cold H₂O [entirely] and not affected by cold soda : add H₂O and soda and shake till small of anhydride is gone and then extract ether & dry CaCl₂. Distill off ether Bu₂B. at 95 mm but residue does not solidify. Oil residue 7 lb. sol. and boils at 200-230° at 14-15 mm with some decomposition [got 7.5 gms distillate]. The dist oil now has no odor of anhydride, is soluble in cold alcohol and separates out the same in 7M as an oil. [Progs. spot quite similar to penta acetyl d. fructose see 57]

59 d. fructose & acetic anhydride. 10 gms Saccharose Ca₂K and 40 cc acetic anhydride heated Bu₂B 7 for 3 1/2 hrs shaking got complete solution [heated in glass 5 hrs] distill off 30 mm Bu₂B. and got 218.7 gms residue with sharp odor of anhydride: add H₂O and shake. This distilled gave 6.5 gms oil bpt 200-230° cflly 210-5° at 16 mm. [bath 280 end]: some formose, acetic anhydride, penta acetyl d. fructose which has never been obtained solid and progs. of it little similar. work in 3 modifs.

[36]

60 Glucose and NaHg. 20 grs Saccharose, 80 grs H₂O and 2 grs PbO₂ emulsified to glucose by heating R.F. bath 103° for 1 1/2 hrs; filter and add 1.25 grs d. tartaric acid (to ppt. Pb) and filter. Now add a solution containing 56 grs Alibory/3 alkali fri Ca. 7. K. in H₂O [total volume being 600 cc.] Cool ice salt to 0° and add a total of 143.75 grs 8% NaHtz C₂H₃K [- 1 1/2 times theory] shaking violently, & adding 1/2 of NaHtz in 1st hr. and then stand over lunch in ice and add rest in 1 hr. Let stand till 5 pm then put in coarse filter and then digest ppt on filter with about 300 cc H₂O & filter again. Total sol is now dist off at 25 mm bath 70° at end and residue in d.f. which still reduces Fehd. sol was distilled 1x with about ale (R.F.) and then filter residue off ale at 25 mm bath 60° for back 17.1 grs gum. This was again heated with 56 grs alibory/3 in 600 cc H₂O and add 143.75 grs NaHtz 8% as before taking 2 hrs to put in NaHtz. Let stand 2 hrs then filter, digesting ppt (alibory/3) with 300 cc hot water, proceeding as before. Residue in d.f. still reduces Fehd. sol was distilled 2x by alcohol R.F. and on dist off ale finally at 25 mm bath 60° and subseq. taking up gum in water and distilling in dry chütz flask at 25 mm. After H₂O was all off and bath was at 190°-230° got much thick water off and on heating higher got more H₂O and gas evolution but no distillate of oxides and residue in d.f. is changed entirely to black tar: ug. to try to distill heavier. Would be better to try to make hexacetyl denit or acetone or Benzald. Cond. products and certainly it is no advantage to use Alibory/3 (see Feb 9 '04) but better use NaHtz in small lots adding each time the thent. amt. Hadory so that solution never gets alkaline.

61 Glucose NaOH phenylhydrazine etc. acc. to Ann 335, 254. Took 10 grs Saccharose 40 grs H₂O and 1 gr PbO₂ and heat B.W.B for 1 hr.; add 0.6 grs d. tartaric to filtrate to ppt Pb and filter again. Make up sol. to 75 cc and add to this in cold a sol of 49 NaOH 25 grs H₂O 70 cc absol ale and 20 grs phenylhydrazine and let stand corked in cold. Let xx of osazone after 24 hrs after 5 days filtered off 17 grs osazone of acetol up to 153° [2 days more standing gave more osazone not weighed] (cf. No. 44)

62 Glucose, phenylhydrazine and 50% acetic, proves that crude glucose contains some laevulose as osazone of glycose is formed. 20 grs d. fructose 80 grs H₂O 2 grs PbO₂ heated B.W.B for 1 hr and add at once a sol. of 40 grs phenylhydrazine in 40 cc 50% Essigsäure. XX of an osazone begin to separate within 2 hours and next day is quite thick. Let stand 24 hrs longer and filter off 11.7 grs crude sticky osazone. This was distilled 2x with 100 cc each C₂H₅ R.F. and last left 6.5 grs insol yellow osazone melting above 190°: must have been glucosazone: some d. fructose is anal. sugars must still have been present [L. d. Biquin removed these from glucose by fermentation] In all the above expts with glucose therefore [58, 60, 61, 55] it must be assumed that some laevulose was still present. [? can sep. from this by sol. of part to acetyl denit in H₂O (?).] (cf. No. 44)

63 Glucose and Benzyl phenylhydrazine; as L. Thorne acc. to Buff. gives a very charact. Benzylhydrazine (9.4.) and glucose was first suspected to be this substance (thet. body), the behav. towards this reagent was studied with neg. result. 20 grs Saccharose 80 grs H₂O and 2 grs PbO₂ heated B.W.B for 1 hr and then add 1.25 grs Tart to ppt Pb. and filter. Distill off H₂O at 30 mm (bath 60°) and take up gum in 100 cc absol ale and filter from osazone. insol gum off bath. Added 25 grs distilled sp. Benzylhydrazine Mpt 201-200° effy 207-208° at 20 mm and let stand in cold for 42 hours; filter from un. amt of gum and distill off alcohol at 30 mm (bath 60°). Got 0 definite on xx to C. C₂H₅ etc i.e. no xx by benzene.

Glucose osazone m.p. 165°

The University of Chicago

64 refr of texture and its behavior towards acetic anhydride (cf 68). Since there is considerable ^{or} ~~swelling~~ ^{browning} in refr of glucose as well as galactose acc. to L. de Bruyn's method tried following method [based on Chro conv to Formose see Nos 14-57] 20 grs Cat K Salicylate, 500 grs H₂O, 2.2 grs PbO₂ and heat in flask (open) BuB. for 12½ hrs. gets yellow almost at once but PbO₂ not all in solution but remains partly as ^{undissolved} PbO(?) at end. Now add 1.4 g d. tartaric acid to filtrate and filter again and then distill off H₂O etc at 30 mm BuB. (bath 70° end). Add 80 cc acetic anhydride and heat on BuB till homog. sol and then BuB R.F. for 4 hrs longer. Distill off at 25 mm BuB + got 168 cc Essigs and are dis distillate. An extracting residue with cold ether + shaking had a fair amt ^{undissolved} gum and Pb salts. Ether dist. off BuB at 25 mm left 25.4 grams oil. [Keep ^{by behavior towards} H₂O etc] (cf 14) ^{1.1 g as good as 586} ~~Acetic acid 207~~ Took 57.2 grs 35% Formalin

65 Formose and phenylhydrazine, and 6) Benzylphenylhydrazine. Took 57.2 grs 35% Formalin of Cat K (20 grs Chro) 492.8 grs H₂O and 2.1 grs PbO₂ and let stand 07 for 5 days but no app. end. ∴ heated BuB. (empty cooler) when PbO₂ prod. present. solution end at end of 4 hrs got no smell of Chro and at end 5 hrs heating solution became faintly yellow. Total heating was 5½ hrs. now add 1.25 grs d. tartaric to hot solution, cool and filter and divide sol into 2 eq. 1st and distill off H₂O etc at 30 mm (bath 60° end). as Now dissolve the Formose 10 grs in 40 cc H₂O and add to a solution of 20 grs phenylhydrazine in 200 cc 50% Essigs and let stand 22 hrs in cold when is ^{pract} solid. Filter after adding H₂O + dry up. yellow 5.5 grs gummy ozon. This was in great part soluble in hot benzene and got beautiful x's needles or rxx for this solvent, up to 160°. A small amt. is far less soluble almost insol. in hot benzene which is probably ~~or~~ ^{acetic} ozon. Results ∴ markedly different from ^{comp.} expt with glucose (see 62)

66 b) dissolve the 10 grs Formose (6) in 50 cc absol alcohol and add 12.5 grs finely dist Benzylphenylhydrazine and let stand in cold for 4 days. Distill off alc at 30 mm (bath 65° end) and heat on boiling up residue 2x with C₆H₆, 5.3 grs ^{brown} insol. gum which was quite sol in cold H₂O and reduces Fehd. solution (∴ sugar present). Benzene solution was very dark and on dist off C₆H₆ at 30 mm (bath 70°) had left 15.5 grs very brown gum which on heating with 70-80° ligrim dissolves only in sun. and [Benzylphenylhydr diastere ∴ should be removed] and on decanting found the gum left is a brown oil ^{pract} insol in water but gave no x's ∴ conclude that Formose or any there can't be present in formose [cf. Ruff Ber 32, 3675].

66 Formose and acetic anhydride. Took 85.8 grs 35% Formalin [∴ 30 grs Chro], 749.2 grs H₂O and 3.15 grs PbO₂ and heated BuB for 7 hours and then added 1.4 grs d. tartaric, filter and divided into 2 parts using 25 ∴ 20 grs for acetic anhydride expt and 1/3 for expt No 67. Distill off at 25 mm (bath 60° end) and dissolve oil left in 80 cc Essig anhydride + on heating BuB got from a homog. solution + then heat 3½ hrs BuB. R.F., distill off now at 25 mm (bath 60° end) and got 60 cc distillate (brown on 50°). Residue in d. f. was dissolved in about 200 cc cold ether filtering from sun. and yellow Pb salt, and then ether removed BuB 30 mm. to dist and of acetate present: got 35.2 grs.

Now heat this oil again B.W.B. 3 hrs. with 35 cc acetic anhydride and distill off again at 25 mm. got back 35.1 grs oil which was now dist at 20 mm. Got I 1.9 grs bpt to 100° at bath 150° II, 9 grs up to 200° (bath 220°) and III 5.4 grs oil bpt 200-220° [bath 260°] leaving 13.4 grs brown tar in d. f. [Had also 2-3 cc acetic anhydride, not condensed, as had no cooler.]
 Redistill I and II using condenser, and got 2.3 grs Essigsaure anhydride bpt up to 50° at 17 mm. and 3.1 grs oil bpt 150°-200° [bath 180-230°] oil very mobile [Keep]. Now put in 7v. III and distill got 8.6 grs oil bpt 200-220 at 17 mm [Keep].

67° Formose, NaOH, phenylhydrazine etc. Took remaining $\frac{1}{3}$ of Formose b) 10 grs. and distilled off at 25 mm (bath 60°). Took up gum in 75 cc H₂O, filter and add to a solution of 4 grs NaOH, 25 g H₂O 70 cc alcohol and 20 grs phenylhydrazine (ann. 335-254) and let stand O.T. corked rubber stopper. next day 21 hrs sep act which increase rapidly in amt. after 6 days filtered off 1.75 grs orange of acetol up to 152°-153°; 7 days later filtered off 2nd crop = wt = 0.3 grs up to 148°-150° [cf 62] (44)
 Oct 1, 06 Nov 11 & Dec 1, 05 Dec 1905 and Jan 2, 06

68 Dextrose H₂O and Cd. 100 grs dextrose 900 grs H₂O and 50 grs Cd. pur. 27 X let stand, shaking at first, sealed with paraffine in a L. flask for 132 days. Vacuum on opening; pour in a $\frac{1}{2}$ L. flask and heat oil bath 120° and pour that 92 cc of distillate contained no trace of CH₃COCH₃ or CH₃COH (by K₂CO₃ etc). Now add a solution of 112 grs CdO 4 H₂ 2 H₂O (they 112.5 gr) to the B.W.B. for 2 hrs [got slight effervescence? Cd formed in reaction], filter and then distill off H₂O B.W.B. means and got 82.5 grs saccharins of H₂O 0.5 (they = 90 grs) The ag. distillates took only 14 grs NaOH quant for neutralization $\therefore$ about 1.6 grs H₂CO₃ must have been formed in reaction (phenolphthalein).

1.08 cc n NaOH for neutralization (phenolphthalein). Treatment with acetic anhydride etc for sep. for lactic acid present in gum is n.g. but was at first done here. The 82.5 grs gum was mixed with 200 cc acetic anhydride and heated 3 hrs at 100° and then 4 hrs at 130°; on distill off B.W.B. at 20 mm had left 140 grs. gum. This shaken 2X in cold with other all dissolved except 21 grs insoluble thick brown gum; the latter was heated again with 40 cc acetic anhydride 2 $\frac{1}{2}$ hrs at 100° and 6 hrs at 120-130° and got on dist off B.W.B. means 18 grs acetylated tar which was insoluble in ether and boiling this off in alcohol $\therefore$ dis covered (much more tar is formed on using Cd than if we use NaOH or K₂CO₃ solutions (see later)).

The other extracts gave B.W.B. in vacuum 115 grs acetylated gums, which was hydrolyzed with 5 grs H₂O at 100° 8 $\frac{3}{4}$ hrs 1 $\frac{1}{2}$ time $\rightarrow$ 85 grs and 2nd time 12 hrs $\rightarrow$ 69.35; and 2nd time The 69.3 grs gums were now digested R.F. 3X with about 1 L acetic ether each time and found only 16 grs insoluble gum is left and on allowing the acetic ether sol. to stand in cold 48 hrs only a very small amt gum separated out, decant from this and det. exact wt. of unol. gums B.W.B. means = 19 grs which on digesting 3 hrs R.F. with 600 cc acetic ether dissolved 3 grs. $\therefore$ now leave & insoluble the 69.3 grs gum only 2 fractions I 53.3 grs sol. in cold acetic ether (3X) II 16 grs gum insoluble therein II is poured later to consist of 1 $\frac{1}{2}$ of tar and rest of saccharins which dissolve with difficulty.

109.5 g lactate 3 hr =
6.05 g free lactate acid

[39]

6.05g free lactic acid [34]
I, 53.3 gms was now heated with 5% H₂O at 100° for 8 $\frac{3}{4}$ hrs to split off traces of acetyl groups and
indict. of Burs in vials had left 50 gms gums. This degraded ^{N.T.} ~~3x~~ with 500 cc ether
gave a total of 14.45 gms gum sol. in ether; ^(3x) on distilling off the ether on W.B. got a separate
oil left (ether extract)
2.9 gms e.p., saccharin up to 160°. The oil left 110 and got

7 2.3 grams crude, or a xx of 1.9 grams c.p., Saccharin up to 100.
 (is 1445-2.3g) was now heated with 40cc acetic anhydride for $6\frac{3}{4}$ hrs at $100^{\circ}-115^{\circ}$ and got
 (see below) (benzene); this oil was treated with 40 cc

27.65 grams aerated gum Burs in vials (still much oily) present; was on the
H₂O and shaken with a solution of 15 grs K₂Cr₂O₇ in 60 cc H₂O then extracted with ether etc.
+ aerated gum which hydrolyzed 3x 8 hrs each at 100° with 5% H₂O gum
+ other for a further separation

Got 13 grams neutral acetyl gum from which by adding acetone and acetone ether got
fully 7.9 grams gum from which by adding acetone and trans para saccharin mainly - was
0.95 grams crude saccharin (2x). The gum left 2 cis and trans para saccharin mainly - was
53 grams; 19 grams left with 3 gm phenylglycidin 100°-110° for 2 1/2 hrs. further etc. just as xx.
53 grams; 19 grams left with 3 gm phenylglycidin 100°-110° for 2 1/2 hrs. further etc. just as xx.
53 grams; 19 grams left with 3 gm phenylglycidin 100°-110° for 2 1/2 hrs. further etc. just as xx.

analysis $Ca^{70} = 9.69\%$ (disappeared) ~~Heavy 9.2~~ ~~rest of salt was now converted by oxalic etc into 2.7 gm. cis and 1.7 gm. trans~~ ~~5.3 grams; 1.7 gm. trans~~ ~~and rest of material was now heated with 1.5 g. calc. 3.0 gm. trans~~ ~~was heated in w.b. to split off acetyl groups and then added 5.5 grams of mobile oil~~

analysis (a) ⁽¹⁰⁾
 parasaccharin [Keep]. V
 The 15 grs K_2CO_3 solution used above was heated in steam
 22.5 grs 35% lab. esp. 10cc etc and extract salt mixture with other juve 5.5 grms of $NaOCl$
 from which got by 5 grs K_2CO_3 etc 5 grms r lactic acid (they about 8 grs) [Keep]:
Acetic ether Extract (feed from 14.45 grs cis stems parasaccharin and r lactic by 3X ether) was contains
 it was found impossible to separate components present by means of Brucin.
 (they 86g) then sol. was neutral and got 2000 vane
 sticky stuff to filler

Acetic ether (1) 35.45 grs saccharins; it was found impossible to
 114 grs Br. salts. This diss in eq. vol. alcohol pour xx needles slowly. There are sticky shreds to filter,
 self/crop I which upon 115-120° melts c. appx. at 135°, on redissolving crop
 with much alcohol 8 grs porous white salt with dect
 dissolved and a cloudy over night

114 grs Br. Salt
Sol 37.55 grs pious salt / crop I 70 grs
Tps 40 cc test alcohol grs in filtering swirling with much alcohol
150-160°. The 8 grs salt in digestion 1 hr R.T. with 50 cc alcohol (lead not dissolved and a residue)
2.1 grs of a pious white powder, depth 165-175°. 7.9 grs Brucine rhombs [formed by dissolving]
24.15 grs, of pious white salt
2 grs Brucine + 9 grs-
the solution

~~The original filtrate was made up by adding H₂O etc.~~
The original filtrate was made up by adding H₂O etc.
The original filtrate was made up by adding H₂O etc.

Saccharine soluble in water. Super white
and finally decolor some much. Super white
Saccharine obtained by with acetic ether solidify thus into a 5.7 grs Ca salt / air dry and 1.1 grs pure
11.295 grs insol. therein. a) pure with CaCO_3 hydrate 0.2 grs more insol Ca salt / p.p. etc.
function with same CaCO_3 etc pure only 2.5 grs Ca salts, combine those salts (2.8)

b) 2.95 gms in alc which on digestion with water
 (∴ sugar or a small gum is present) b) gave only 2.9 gms in alc
 and digest K₂C₂O₄ ppt again and got total of 7.5 gms Ca salts. The salt of ferrous in
 not measured; analysis as dry found Ca = 8.78% then for Ca(C₆H₁₁O₆)₂ 2H₂O = 9.2
 gms to 4.7 gms succhain by oxalic acid etc and on digestion with
 ferrous ∴ converted back by 8.9 gms B₂O₃

at 90-110° turned red by turning back to 47° fresh water; got no x lls on Hauding; curd edn made
the salts left were now converted; got no x lls on Hauding; curd edn made
red after 2x found 43 gms dissolved; got no x lls on Hauding; curd edn made
to remain salts [13.3 gms]. This chocolate in 50 cc absol. alc R.F. left 1.1 gms insol
over 4 fibres " up to 170-174° none xx these from 1 cc tho at 200°C
alc not in C.R. after 6 weeks 0.5 gms purple distn.
Nashua Oct 176-180.

The alc sol. from 1.1 ps woody fibres got in standing 6 weeks in C.R. entirely solid (discarded)
Crop II. The orig. alc. filtr from 37.55 ps Buein salts crop I gave on standing and conc. etc
 24.15 ps salts, Crop II, softening 110-140° stiffen at 140° sticks must like crop I, this was dissolved in
 H₂O & K₂C₂O₄ from over H₂O in conc. got 23 ps salt up to 110-115° stiffen 135° (discarded)

Crop III alc. filtr. from crop II & I were entered sol. in H₂O & K₂C₂O₄ etc got 33.6 ps salt which dissolved
 in 30 cc abs. alc. sol. stand grad. got solid in 6 weeks in C.R. (discarded).

Part insol. in acetic ether II. Took the 16 ps insol. gum in 5 pts H₂O & heated 100° for 8 3/4 hrs. 6

split off c₂c₃ groups etc got 15.6 ps gum. This was separated by 2x extraction with
 acetic ether into 7.95 ps soluble and 7.65 ps insoluble gum. The latter digested 10 hrs 100-180°
 with 29 cc acetic ether only & gave 12.65 ps acylated gum of which 3.4 ps black tar insoluble
 in R.F. in 100 cc ether was discarded. The ether extract hydrolyzed 3x by 5 pts H₂O at 100° for 8 3/4 hrs & gave
 finally 5.6 ps gum. Now convert the 7.95 ps gum + 5.6 ps gum separately by CaCO₃ etc
 into Ca salts after 4 hrs etc got 11.82 ps Ca salts (an dry 24 hrs) analysis = 7.83% Ca

Now convert Ca salts left to 7.5 ps saccharin gums by oxalic acid & son digestion found this in
 the main part into acetic ether R.F. (fill but 2.2 g). An emulsion thus gave Buein salt got

no separation ∴ n.g. in portion heated with 3 pts phenylhydrazine at 100° etc gave gums only ∴ n.g.
 Oct 9 - Nov 1 - Nov 6 - Nov 13 - Nov 24 - 1905.

69 Lactulose H₂O and CaO. 100 ps Lactulose 900 ps H₂O and 50 ps pure CaO stood 139 days in
 cold. Now heat 100° for 6 hrs and add 112 ps conc. H₂O (pure CaO) & sol. of ag. filtr in conc.

a weighed amt of H₂O & found that total ag. dist took only 16 cc 10% NaOH to make alkaline.
 gum left in d.f. = 83.5 ps (they 90 ps to H₂O 05). Heat this with 100 cc acetic ether divide 2 1/2 hrs at 100° and 5 1/2 hrs
 at 120-130° & got 136.5 ps acylated gum which on shaking 2x cold & 2x R.F. with ether left 18.5 ps
 insol brown acylated tar (discard). The pale yellowish gum sol in ether = 118.5 ps was heated
 100° 2x for 8 3/4 hrs → 90° and for 12 hrs → 73 ps with 5 pts H₂O & 3 1/2 hrs (pure gum) 71 ps gum.
 The gum was digested 2x with 600 cc acetic ether R.F. and had only 14 ps left insoluble;
 but on standing over night a small amt more of insol. gum came out.

Now have 2 portions gum, I, 55.6 ps & II, 15.4 ps insoluble gum.
 I. Dissolved a part of gum I in H₂O and made various expts with it. 1° Ca salt after 4 hrs etc gave
 10.76% H₂O, and then 11.09% Ca then 10.02% for Ca (C₆H₁₁O₆)₂

2° Basalt after 4 hrs etc gave 7.61% H₂O (100°) and then 30.4% Ba then for Ba (C₆H₁₁O₆)₂ 27.27
 3° guinine salt melts low & is very soluble 4° p. n. benzyl alcohol at 100° gave a definite
 5° benzyl phenylhydrazine at 100-130° gave 0. 6° p. b. etc gave a very gummy & sol. salt.
 7° dodo K salt as 6° 8° dodo NH₃ ag or a.t. 100° 9° cinchonin salt is gummy & very soluble.

10° morphine salt melts at 85-135° is very soluble (sol. family acid) 11° Buein salts work better ∴ took 10 ps
 gum & convert by 24.3 ps pure Buein salt 42.5 ps Buein now. This dissolved in 42 cc hot
 alc. and on standing 3 days got semi solid. Filter through sticky salt 7.9 ps crop 2 up to 154-8°
 after drying 3 hrs in conc. H₂O. On digesting this salt R.F. with 50 cc abs. alc. found it
 in great part insoluble ∴ filter got 5.4 ps dops 172-4° this salt is very sol. in H₂O ∴ diss it
 in 4 cc H₂O and 40 cc alc. & stand 5 days got 2.45 ps of woody fibres
 in nodules made up of needles with deft 177°

17/11 may ^{also} be cis para saccharin

body ~~mostly~~ is a space isomer ie saccharin or is saccharin. The ale mother liquors all combined gave 33.6 grs salt which in xx from ale gave no separation i.e. unite with comp. lot from experiment No 12

No 12; Now repeat 11° using 21 grs gum + 49 grs Borneo + 177 grs Borneo salt; this warmed with 100cc ale, filtered hot speared ppt with 125cc warm ale gave 13 grs Borneo salt with deft 172-4 (after drying 4 hrs in vacuo). This salt was converted by 5.35 grs Bu₂SO₄ into 9.1 grs Borneo (3x conc 30% 100°) and into 3 grs saccharin gum (2x acetic ether); this gum on long standing gave some xelle of saccharin but main part remained a gum.

Now proceed with rest of material (incl 3 grs saccharin gum) as follows; convert all the Borneo salts left from 11° & 12° by Bu₂SO₄ etc 55.6 grs Borneo and 21.5 grs saccharins which with 3 grs saccharin gum mentioned makes 24.5 grs saccharins. Heat with 75cc acetic acid & boil for 6 hrs at 100° & for 8 hrs at 120-130° and got 40.6 grs acetylated gums which dissolved easily leaving 3.7 grs black tar, in cold ether on shaking 2x. The ether sol. was shaken with 10 grs K₂CO₃ in 100cc H₂O etc and got 32.2 grs neutral acetylated gum; the K₂CO₃ solution on working up by boiling 4 3/4 hrs gave 100cc cold ether i.e. gum by ex to c. ale 3.2 grs gum of which 1/2 dissolved easily on shaking 2x with 100cc cold ether i.e. gum is elastic and rest is saccharin gum with inf speared.

The neutral acetylated gum 32.2 grs hydrolyzed 3x by 5 pts H₂O (8 hrs 100°) gave 20.1 grs saccharins. These taken up in imm. ant warm acetic ether solutions gave 15 grs saccharins as pure saccharin m.p. 160°. The acetic ether solutions evaporated gave 14.3 grs Ca salts (as dry 40 hrs) analysis Ca = 90.04% Ca (as phosphate). (discarded rest of salt)

II Part insol in acetic ether = 15.4 grs. As the gum still contains sugar and some tar this in part 1/2 sol in acetic ether attempted to get something definite by conv. to Borneo salt but n.g. i.e. converted gums; this left 3 grs insol brown tar on shaking 2x with cold ether and the acetylated gums. 15 grs (in ether) gave on hydrolysis 3x with 5 pts H₂O (12 hrs) gave 9.3 grs saccharins. This with Ca CO₃ etc gave 8.65 grs Ca salt as dry (48 hrs) (discarded)

70 Sweet sugar and lime & H₂O. Took 100 grs cane sugar 200 grs H₂O and 2.5 grs CrO₄ H₂ 2/H₂O and heated R.T. 3 1/2 hrs on 12 hrs. for hydrolysis sol. gets yellow (cf. Paligot.) and 450 grs H₂O cool and then add 50 grs pure lead total paraaffine shot then 1 week shaking time to time. Now open and heat in oil bath 100° R.T. for 8 hrs & then add a sol of 109.5 grs CrO₄ H₂ 2/H₂O & heat. Got 89 grs gum from ag. filtr. The ag. dist. took 20 cc 10% NaOH to make alkaline (roughly done). Digest the 89 grs gum with 210cc acetic anhydride 3 hrs at 100° and 4 hrs at 120-130° got 137 grs acetylated gum. This taken up in ether 3x R.T. left 34 grs insol tar & got from ether 107 grs acetylated gum Borneo then this was hydrolyzed 2x at 100° with 5 pts H₂O 11 1/4 - 17 1/2 hrs got 67 grs gum which was separated by 2x deposit with acetic ether into 52 grs I, soluble and 15 grs II, insoluble.

I 52gms heated again with 5 lbs H₂O & 8 lbs at 200° now became 48.5gms gum. and II heated same way for 164gms
On dissolving I in 46cc acetone shaking stand for a separation of 5.45gms saccharine, crop I,
melt 157-60° which xx from 125cc hot acetone gave 3.15g crop body and on cone. filter got 2.04gms more
up. body (melt 160°). The acetone solution on cone and dry acetic ether gave 1.65gms more
saccharin xxlle, crop II. Now distill off acetone etc but was got 41gms saccharin gums
which heated with 123cc acetic acid by distill for 10 1/2 hrs 100-125° etc gave 64.5gms acylated gums.
This was taken up in cold ether decanting from sin. and wool brown tar and then washed with
a solution of 20gms K₂CO₃ in 200cc H₂O. Got 48.2gms neutral acylated gums and the K₂CO₃
solution heated but still did not etc gave 7gms gum which on shaking 3x with 100cc cold
ether dissolved 4.5gms others with K₂CO₃ etc gave only 2.35gms of this lactate 3rd (keep).
The acylated gum (neutral) hydrolyzed 3x 9 hrs each 100° with 5gms H₂O gave 29.7gms gum,
which was heated with 10gms CaO 3rd H₂O K₂CO₃ etc got 31.2gms Ca salt air dry (64 hrs).
analysis 9.6% Ca; now convert back by oxalic etc to 20gms saccharin s. On digesting
this R.F. 6x with 300cc ether found 10.5gms dissolved. The total ether extract was
now shaken for 3 days in cold with about 900cc ether and decanted from gum & xxlle and
found that 7.4gms had dissolved K₂CO₃ in vacuo. This must be mainly cis and trans
para saccharin. Digest this with H₂O and 16.5gms Buein (theory for 6.8gms sacch) and found
sol. is still acid. got 23.5gms Buein salts B₂O₃ in vacuo which was dissolved in 24cc. This
last abso. alcohol and got on standing 6.55gms of a gum xx ppt with melt 172-178°. This
on dissolving in 75cc abso. etc R.F. gave on standing over night 1.9gms + 1.37gms crop II of
Buein cis para saccharin melt 180-192° (keep)
The ac. filter from 6.55gms salt gave 14.65gms of very low melting (and very sol. Buein
trans para saccharin etc. got from this by K₂CO₃ etc 9.2gms Buein and
4.2gms trans para saccharin whose behavior towards HNO₃ dil was studied Mch 8 '06 [see No 91]
The total acetic ether extract, freed from cis and trans para saccharin by ether, now
weigh 12.4gms; they must contain 2.1gms isosaccharines and a new saccharin immiscible with
ord. saccharin. The 12.4gms were heated with H₂O and 26.7gms Buein got (sol in alkali)
35.8gms Buein salts. On dissolving this in 5cc H₂O and 120cc etc and letting stand in C.R. for 10.3gms (crop I)
decant cone group. Wash with deph 100-110° after drying H₂O vacuo got 9.5gms salt with deph 120-130°
these rexx from 5cc H₂O and 95cc etc gave 0 but on cone got 3.7gms needles melting 95-100° melting 105-110°
and after at 114-5°. The ac. filter from 19.7gms (the 10.3gms decant Wash (crop I) on cone gave crop II 19.4gms
needles same as crop I. Crops I & II (isobutene) removed by 2 washes K₂CO₃ etc into 11.9gms Buein the H₂O
and into 4.8gms saccharin (acetic ether extract). This on long standing did not xx; converted it
by CaO₃ etc to Ca salt and on cone ag. sol and scratching got 1.81gms isosaccharinate xxlle
to separate out [keep]. The ac. filter from crop I & II gave aummy Buein salt on cone
over H₂O in vacuo which gradually fits solid (discarded).
II Insoluble Portion = 16.4gms was found on digestion R.F. with acetic ether by distill & sheeted 1/2 lbs at 120-130°
insoluble gum; the latter was heated with 27cc boiling acetic acid by distill & sheeted 1/2 lbs at 120-130°
got 14.6gms acylated gum which on digesting 5gms H₂O & 8gms 100° 6.9gms gum.
K₂CO₃ etc etc to get rid of some sugar present.

164gms
weight of gum lactic by ph. by J. in alc sol.

The University of Chicago

got a total of 11.7 grs Ca salts air dry 24 hrs which by analysis gave 8.3% Ca.
 Now regenerate the saccharins from these by oxalic etc & got 8.1 grs from which on 2x
 digestion with 20 cc acetic ether brewed 5.3 grs gum from which could get no
 saccharin x'lle in standing; next mixture with alc got 2.3 grs more: total 7.6 grs
 This was treated with 15.8 grs Baume in wks. (thing for 6 1/2 grs Sacch) neutral sol. gave 23 grs salt
 Buns verno. This x' from 7cc H₂O and 95 cc alcohol gave no x'lle 4 weeks in CR: i distill
 7 1/4 of alc let stand 2 weeks CR. but got 0.1 gr. 1 set free saccharins etc by KOH
 and got 6.1 grs (discarded). It is obvious from above that cis and trans para saccharins
 α and β saccharins and α and β isosaccharins are found from levulose, hex tene, Mannose
 or invert sugar [brides lactic acid & loby C₆H₁₂ Ba₂H₂ KOH NaOH etc.
 Nov 29 05 and Nov 19 06]

710 Dextrose and 7 1/2 % NaOH. (almost 7 units)

Took 50 grs dextrose (mp 148-90), 12 Hrs and 74 grs NaOH added by alc let stand in S.T. for 15 days
 O.T. and then heat in bath at 50-60° for 26 3/4 hrs. Only slightly colored solution: add 192.5 grs 35%
 lab. HCl & distill off Buns verno. Shake up residue in cold abso. alc leaving 103 grs NaCl (thing 108)
 amt guminal = 35 grs Buns verno. O.T. this in bath 100-120° for 13 1/2 hrs with 105 cc acetic anhydride
 and got 53.5 grs acetylated gum which taken up in 3/4 l. cold ether left 5.1 grs tar + NaCl.
 The ether solution washed with 20 grs K₂CO₃ in 20 cc H₂O etc gave 23 grs saccharins.
 gums which hydrolyzed 3x 4 hrs w^o with 5 H₂O gave 23 grs saccharins.
 The K₂CO₃ solution with HCl etc gave 7.3 grs gum 1/2 lactic + saccharins.
 The 23 grs saccharins taken up in H₂O & treated with Baume etc gave 0 definite: set
 free saccharins again = 16.2 grs [Keep] there must contain much para saccharins;
 and should: first be digested R.T. with other etc. dissolved Oct 9 '07

720 r. lactic + acetic anhydride.

5 cc lactic 1.21 and 20 cc acetic anhydride were heated in a S.T.
 w^o for 11 hrs & distill off Buns verno got 6.9 grs gum; reheated this with 15 cc acetic anhydride
 R.T. 130° for 7 hrs & got 6.9 grs gum Buns verno, a few drops of this dissolved at once in the
 & effervescence with Na₂CO₃ solution. Distilled the salt at 23 mm and got about 0.5 cc oil bp 65-85°
 & finally gum. amt from 185-210° (bath outside 280°); total dist = 6.3 grs & gum. salt in d.f.
 Repeated this expt & got 6.2 grs gum: add 20 cc H₂O shake when oil all dissolved; now
 add 5 grs K₂CO₃ in 20 cc H₂O and heat Buns for 1 hr and then add 7.5 grs 35% HCl etc and
 got 4.8 grs r. lactic with other which on treatment with 5 grs ZnO₃ etc gave 5.7 grs
 r. lactic 3 H₂O theny about 8 grs: O.K.
 H₂ 1.96 in r. lactic and on glycollic acid; took 2 grs each of glycollic & lactic acids
 and heated S.T. for 11 hrs with 8 cc H₂ 1.96 & 1/2 grs P. Add the ext. c. ether & dry
 Cal 2. in case of lactic got about 3 cc oil smelling strongly of propionic acid but
 probably containing some & 10 propionic acid;

(44)

In case of glycollic acid got strong smell of acetic acid but found no lactic acid although traces might have been overlooked

Oct 4 05; May 18 06

74° Glycollic acid + acetic anhydride. 5 grs glycollic acid and 20 cc acetic

-anhydride heated in S.T. 11 hrs Kek. 100° and got 7.6 grs gum Burz vane; heated again with 15 cc acetic anhydride at 130° for 7 hrs & got 7.5 grs gum Burz vane. a few drops of the gum dissolves easily in H₂O and solution effervesces with CO₂ Na₂; on distilling at 22 mm the greater part

boils from 175-183°. A fresh experiment using 5 grs glycollic acid and 15 cc acetic anhydride and heated in bath at 100° for 8½ hrs gave 7.7 grs gum Burz vane as a mobile oil. The oil dissolved almost instantly on adding 10 cc H₂O & shaking; now add 20 cc soda solution (lab neg) & let stand 5 minutes & then acidify c. dil H₂SO₄ and extract 3x by ether & dry CaH₂ etc. Got 5.1 grs oil Burz vane which is probably acetyl glycollic acid; the body gets solid on scratching at once and can be xx from ether by adding much ligum. It comes out in needles which melt from 68°-70° [keep].

of Oct 4 05 & 5 05 March 1 06 and May 17 06.

75° r. Glyceric acid and acetic anhydride. Heated 144 grs Ca7K glycerinate in Burz vane and weight went down to 12.3 gr. This was heated R.T. 100-130° for 8 hrs with 49.2 g acetic anhydride & then got 20.9 grs gum Burz vane. This dissolved except 4.7 grs in cold ether; on distilling 7 of the other in Burz vane, the oil caps dissolved at once on adding eq. soda solution & on ext to this with ether got pract 0 but an acid from with dil. H₂SO₄ etc. got an ext. 2x with ether a large amt of oil; O.K.

Repeated expt. with op. glycerinic acid made from 20 grs op. Ca glycerinate up to 135° & xalac acid etc. getting 14.6 grs acid & heat this with 45 cc acetic anhydride in oil bath 100-120° for 8½ hrs. Got 26 grs solid gum which all dissolved except 1½ g in cold ether (450 cc); the ether sol. shaken with 20 grs K₂CO₃ in 20 cc H₂O & got 0 left in ether. Heated the K₂CO₃ solution in Burz vane for 5¾ hrs (and then 100° for 30 grs-35° for 10 cc) and take up residue in ether (leaving 17.2 gr K₂CO₃) and found 13.7 grs gum. This digested with 100 cc CO₂ & the gum 6.5 grs op. Ca glycerinate crop I and 3 grs crop II which was sticky (not pure). O.K. but some slight smearing of r. glycerinic in operation.

Took a new lot of op. glycerinic 5.3 gr Burz vane and heated it 100-90° for 9½ hrs with 16 cc acetic anhydride and got 8.7 grs colorless gum Burz vane. On shaking this for 5 minutes with 30 cc H₂O it all dissolved and got by ext to sol 3x by ether etc 7.4 grs oil back again (Burz vane). This oil was now dissolved in 10 cc H₂O and 20 cc lab. soda solution (and dil H₂SO₄ etc ext 3x by ether and got 6.8 grs gum Burz vane. This oil was shaken next day with 30 cc H₂O but did not all dissolve; heat 8 hrs at 100° R.T. to hydrolyze gum. got 4.1 grs gum Burz vane & 4.5 grs op. Ca glycerinate; 2 1/2 grs. O.K.

CaCO₃ etc gave very large amt of op. Ca glycerinate; look 4.6 grs d. glucose Burz vane & heated it with 18.4 grs acetic anhydride for 8 hrs at 100-130° & got 7.4 grs gum Burz vane which dissolved on shaking in cold ether (except 1 star). The gum left after drawing off the ether was a viscous slightly colored liquid; added soda solution to it and shook for one hour then ext to c. ether & dry CaH₂ etc & got 3.3 grs neutral oil.

76° Glyceric acid and acetic anhydride; look 4.6 grs d. glucose Burz vane & heated it with

The University of Chicago

77° Maltose & CaO & H₂O. Took 40g Maltose (pure 112-15° & efferv 135° C at K) and 400cc H₂O + 20g powder
 CaO (COTK) and let stand in sealed flask for 163 days (shaking). Now heat in oil bath 100° for 7 3/4 hrs +
 then add a hot sol. of 44.8 gms oxalic acid 2H₂O (highly efferv) to digest & filter. Total H₂O dist lost 6.5 cc 10% NaOH
 to make alkaline (roughly done). Got 35gms brown gum Burz vane (theory 36g for C₁₂H₂₂O₁₁). This was digested
 with H₂O and CaO 3 1/2 gms + got 5.75gms insol Ca salts and 2.2gms C₂O₄; the aq. filtr. came to about 100cc
 gave 4.9gms + 1.6gms Ca isosaccharinate dried 100° which with oxalic acid gave 4.95gms pure isosaccharin
 melting 80°-92°. It is but xx from about 80cc acetic ether and got thus 3.2gms sp. body m.p. 95-6° & filter
 on cone. gave 1.05gms more upon 94°-50° crop 0.09gms but m.p. 88°; O.K.
 The aq. solution from crops + the Ca isosacch. gave on add. of alcohol a gum; take up in H₂O & ppt.
 Ca by oxalic acid got 29.2gms gum Burz in view. This was heated with 75cc acetic anhydride
 2 1/2 hrs at 100° and 4 hrs 125-130°. Got 47.1gms acetylated gum which on extracting 3x ether 2x R.F. gave 9.7gms
 insol. brown gum. Oil left in ether now det as 38gms Burz vane. This was hydrolyzed 1 1/2 hrs with 190cc
 H₂O gave 28.5gms gum; hydrolyzed again 12 hrs 100° with 142.5cc H₂O and got 23gms gum (keep) still contains
 a lactic. might do well to work this up for **β isosaccharin** (see if any saccharin in product) (COTK);
 lactose, CaO, & H₂O. Took 40gms lactose (O.T.). Heat in bath at 100° for 7 3/4 hrs & then add a sol. of 44.8gms
 oxalic acid 2H₂O (pure efferv. : cor?) & filter & wash Burz vane. Total aq. dist lost only 6cc 10% NaOH to
 make alkaline (roughly est.). Got 36.5gms brown gum which with 50cc H₂O and 11.5gms CaO 3/4 gave
 4.6gms insol Ca salts and 2.1gms C₂O₄; aq. filtr. came to about 100cc & gave 2 crops of Ca isosaccharinate,
 5g + 1.4gms. This by oxalic acid gave 4.95gms pure isosaccharin m.p. 80°-92°, but xx from 80cc acetic ether
 got 3.14gms sp. body m.p. 95-6° and then 0.45gms more 94°-95° and 0.2gms m.p. 88° + sum of gum dis. and sol.
 this isosaccharin mixed with one from maltose (was wash. m.p. 95-6°) is identical.
 Aq. filtr. from Ca isosacch. is now pptd by Oxalic acid & got 18.9gms gum. This hydrolyzed with 75cc
 acetic anhydride 3 hrs 100° and 5 1/2 hrs at 125-130° gave 6.1gms acetylated gum. Dissolved this 2x R.F. in
 ether and found 13.5gms insol brown tar. Total oil in ether now det Burz vane as 38gms.
 This was hydrolyzed 7 1/2 hrs 100° with 5 1/2 H₂O & got 27gms; 2nd hydrolyzed 16 1/2 hrs above gave 21.9gms gum (keep)
 still contains v. lactic acid. must contain α and β metasaccharin & also β isosaccharin.
 & gave no 2gms standing 16 1/2 hrs metasaccharin xx m.p. 145°
 40g
 20g
 20g

78° Lactose, CaO, & H₂O. Took 40gms lactose (O.T.). Heat in bath at 100° for 7 3/4 hrs & then add a sol. of 44.8gms
 oxalic acid 2H₂O (pure efferv. : cor?) & filter & wash Burz vane. Total aq. dist lost only 6cc 10% NaOH to
 make alkaline (roughly est.). Got 36.5gms brown gum which with 50cc H₂O and 11.5gms CaO 3/4 gave
 4.6gms insol Ca salts and 2.1gms C₂O₄; aq. filtr. came to about 100cc & gave 2 crops of Ca isosaccharinate,
 5g + 1.4gms. This by oxalic acid gave 4.95gms pure isosaccharin m.p. 80°-92°, but xx from 80cc acetic ether
 got 3.14gms sp. body m.p. 95-6° and then 0.45gms more 94°-95° and 0.2gms m.p. 88° + sum of gum dis. and sol.
 this isosaccharin mixed with one from maltose (was wash. m.p. 95-6°) is identical.
 Aq. filtr. from Ca isosacch. is now pptd by Oxalic acid & got 18.9gms gum. This hydrolyzed with 75cc
 acetic anhydride 3 hrs 100° and 5 1/2 hrs at 125-130° gave 6.1gms acetylated gum. Dissolved this 2x R.F. in
 ether and found 13.5gms insol brown tar. Total oil in ether now det Burz vane as 38gms.
 This was hydrolyzed 7 1/2 hrs 100° with 5 1/2 H₂O & got 27gms; 2nd hydrolyzed 16 1/2 hrs above gave 21.9gms gum (keep)
 still contains v. lactic acid. must contain α and β metasaccharin & also β isosaccharin.
 & gave no 2gms standing 16 1/2 hrs metasaccharin xx m.p. 145°
 40g
 20g
 20g

79° Cane sugar and CaO & H₂O. Took 260gms 35% C₁₂H₂₂O₁₁ solution i.e. 90gms C₁₂H₂₂O₁₁ and 2238gms H₂O
 and 9.45gms p.p.t. and heated 8 hrs Burz R.F. & then added 5.7gms tartaric acid & cool & filter & then
 add 45gms powder CaO (COTK) seal and let stand (shaking) for 137 days. Heat Burz for 5 3/4 hrs
 & then add aq. sol. of oxalic acid 2H₂O 10.8gms, digest filter etc. Total aq. dist requires 4 gce
 10% NaOH to make alk. solution roughly est. Got 71.5gms brown gum, which was digested with
 200cc acetic anhydride 2 1/2 hrs at 100° and 6 hrs at 120°-130°. Got 103gms acetylated gum which on
 digesting 5x with ether left 29.8gms brown brown tar (discarded). Found in ether 71.5gms acetylated gum
 which was hydrolyzed 1 1/2 hrs at 100° with 5 1/2 H₂O & gave 50.5gms gum. Hydrolyzed again 12 hrs 100° & got 45gms gum; on
 digesting this 2x R.F. with 300cc acetic ether, found only 9.1gms insol brown gum (keep this
 in H₂O solution) acetic ether ext. dist off Burz vane gave 34.5gms gum (keep).
 (must contain v. lactic) & is saved Oct 2/7

80° Formose C₁₂H₂₂O₁₁ & H₂O. Took 260gms 35% C₁₂H₂₂O₁₁ solution i.e. 90gms C₁₂H₂₂O₁₁ and 2238gms H₂O
 and 9.45gms p.p.t. and heated 8 hrs Burz R.F. & then added 5.7gms tartaric acid & cool & filter & then
 add 45gms powder CaO (COTK) seal and let stand (shaking) for 137 days. Heat Burz for 5 3/4 hrs
 & then add aq. sol. of oxalic acid 2H₂O 10.8gms, digest filter etc. Total aq. dist requires 4 gce
 10% NaOH to make alk. solution roughly est. Got 71.5gms brown gum, which was digested with
 200cc acetic anhydride 2 1/2 hrs at 100° and 6 hrs at 120°-130°. Got 103gms acetylated gum which on
 digesting 5x with ether left 29.8gms brown brown tar (discarded). Found in ether 71.5gms acetylated gum
 which was hydrolyzed 1 1/2 hrs at 100° with 5 1/2 H₂O & gave 50.5gms gum. Hydrolyzed again 12 hrs 100° & got 45gms gum; on
 digesting this 2x R.F. with 300cc acetic ether, found only 9.1gms insol brown gum (keep this
 in H₂O solution) acetic ether ext. dist off Burz vane gave 34.5gms gum (keep).
 (must contain v. lactic) & is saved Oct 2/7

- (81) Isosaccharin (α) and Anilin, of broken Jpr 6/37 3/8; proved that isosaccharin reacts very slowly with anilin at 200° or above. Thus 1 g. isosaccharin + 1 g. anilin heated 5 hrs at 95-105° gave product in action: heat mixture 130-140° for 2 hrs then added 2 g. more anilin and heat 140° for 1 1/4 hrs. add other solid stand over 0.9 g. isosaccharin up to 88-95° to xx out. Now heat 1 g. isosaccharin + 3 g. anilin in bath at 180° for 2 hrs and got by adding other etc 0.7 g. isosaccharin up to 88-95° or xx from acetone other heat up to 95°-100° in action. Now took 1 g. isosaccharin and 3 g. anilin + heated in bath at 235° so that anilin run up test tube. Now got by other etc 0.8 g. gray, sublimates at 90° & melts from 115-120°. On dissolving this in 2 cc alcohol got xx of isosaccharin mixed with xx needles of isosaccharin anilide which picked out melt at 150-155° ∴ reaction still incomplete but well adapted for identification of isosaccharin (mod.)
- (82) Binein salt of isosaccharin, made from isosacch (1 g) and Binein 2.43 g. etc ext. 1x by crystals and distilled off H₂O at 60° in vacuo got 4.5 g. white xx needles. This dissolved in 15 cc absd alc & on standing got 1.9 g. xx plates which on drying cp. almost entirely melt at 100° leaving H₂O then got lower again finally melt 140-145°. 1st after drying H₂O in vacuo is 1.8 g. sublimates at 152-3°. alc. mother liquor wraps over H₂O in vacuo gave 1.1 g. white xx lvs (melt 140-42°). The salt can be best purified as follows: take 2.2 g. in 2 cc hot H₂O and add 40 cc alcohol when got on standing in c.R. magnificent rhombs clear as glass, very heavy, 1.3 g. & found depts of best selected xx lvs is 149-150° (slow heating) [keep].
- (83) Phenylhydrazine of isosaccharin (see Kilian's Soda). Took 1 g. isosaccharin and 3 g. phenylhydrazine and heated to 130-140° in bath for 3 1/2 hrs (too long & too high). Mixture got very thick on cooling & was not usual colored; add other stir & got solid got 1.8 g. up to 108-115°. Body is very soluble in H₂O & stiff. sol in acetone other. Comes out from acetone other as an oil which afterwards solidifies; this solid is absd. alc. Took 1.5 g. in 4 cc hot alc shd and on standing on night got 1.25 g. radiating needles with upper surface rounded like shot up to 116-117°. Next this from 3.5 cc alcohol and got 1.8 g. up to 117-118° after drying 2 days in vacuo [ready for analysis].
- (84) Isosaccharin and benzoyl chloride & p. nitrobenzoyl chloride; heated 1 g. isosaccharin to mols c. soda dry call. got 3.6 g. gum much above not got solid ∴ n.s. (body is easily sol but alc seems not in cold alc). a similar exp with 1/2 gram isosaccharin and 1.75 g. p. nitro (7 mols) in 10 cc H₂O and heat 100° for 10 minutes cool & decant. Took 1 g. isosaccharin (6 mols) & shook well up when reacts at once got much insol oil. and then add 5.2 g. benzoyl chloride (6 mols) & shook well up when reacts at once got much insol oil. On adding H₂O ext. call. working c. soda & drying call. got 3.5 g. of an oil which is partly xx. Body is quite sol in cold alcohol and different from oil obt. from free isosacch. & Benzoh. (see above); it is probably a mixture.
- (85) Binein salt of α saccharin. Took 0.5 g. α. saccharin up to 160° (from dextrose & CaO) and 1.2 g. Binein about H₂O & pump Binein into 17 cc then got rhombs xx lvs 0.85 g. up to 135° after drying in exp. on cooling & comes out ∴ one to 17 cc then got rhombs xx lvs. of salt ∴ n.s. ∴ deposit again with H₂O. This was found to be Binein formed this dissolve. of salt ∴ n.s. ∴ deposit again with H₂O. To get back salt; salt obt. is very sol. in cold H₂O and addition of alc gives a porous white powder with depts 152°. Now took salt and dissolved it in 0.7 cc H₂O and add 7 cc alcohol shd stand 6 xx. got opaque needles grouped in disks with soft and woolly woolly fell 0.4 g. with depts 153°. After drying 18 hrs H₂O in vacuo.

86° Phenylhydrazide of α saccharin (cf Fischer, Ber 22 2728) Took 18 saccharin and 3 grs phenylhydrazine and heat in bath 3 hrs from 110°-134°. Cool, add ether, got a gum which got solid on scratching. 1.39 grs mpt 158°-165°. XX it from 200 cc acetone ether and got 0.9 grs needles aggregated in flocculent masses mpt 167-9° (keep) is very sol in absolute alcohol.

87° Solubility of α saccharin and of α isosaccharin in ether: took 1.5 grs isosaccharin. Sprayed heated R.F. 1 1/4 hrs with 500 cc ether; decant best and found 0.7 grs insol isosaccharin and on cooling the ethereal solution deposited about 0.3 grs isosaccharin XXlle in beautiful transparent XXlle. Solubility is very slight. Took 3.3 grs pure α saccharin mpt 160° heated R.F. 4 hrs with 500 cc ether decant best and found 2.75 grs pure saccharin. This body is less sol. even than α isosaccharin. α Saccharin is insoluble in hot benzene, very sol. in water, and alcohol and can be but XX fine hot acetone as it is only slightly soluble in acetic ether taking: too much solvent (see No 70).

88° α Saccharinate; took 18 grs α saccharin (mpt 160°) and deposited H₂O 0.5 grs pure CaCO₃ etc and ppt Ca salt by alcohol. got a porous white salt which swells up much in mpt at 90°-100°. analysis after 24 hrs air dry = 8.72% Ca (as CaSO₄) theory for $(C_6H_{11}O_6)_2 Ca \cdot 2H_2O = 9.2\% Ca$.

89° Galactose, CaO & H₂O [cf. Det. 6, '05 Nov. 14, '05 Jan. 3, '06 Feb. 1, '06]. 100g galactose, 1/2 H₂O, 50 grs pure CaO (C₆H₁₂O₆) was mixed & shaken (slightly efferv. 200 grs), decant 112 grs CaO 4 H₂O (Schubert 74 eq. filt. in vacuo Bux). The total eq. dist took only 13.5 cc 100% NaOH to make alkaline (nearly done). got 80.5 grs gum which was digested with 200 cc acetic acid & 8 hrs at 100° and 4 hrs 120°-130°; got 123g aerated gum which digested 3x cold 3x hot they gave 35.5 grs insoluble tar! Found that after exl. cont. 90 grs aerated gum; this was hydrolyzed with 5 pts H₂O 8 1/2 hrs gave 63g when again 11 hrs 5 pts H₂O & got 54.5 grs gum. This was digested R.F. 4x with 200 cc acetic ether and found total of 28.6 grs I dissolved, leaving: 25.9 grs II insoluble - proved on investigation to contain traces lactic acid & saccharins namely α and β meta saccharin and cis and trans pure saccharin (as meenates). Took II 25.9 grs insol gum & removed by H₂O and 10 grs CaCO₃ into 28.35g Ca salt (ppt) by alc tar dry 48 hrs; swells up 90°-110°. analysis Ca 8.34% - theory 2H₂O 9.2%.

Now convert Ca salt back by oxalic etc into 18.8 grs gum which on diss in 100 cc alc & let stand gave no XXlle of α meta saccharin. Then heat it with 41.5 grs Buxen (theory 43) & trap Bux3 vacuo & got 62.9 grs salts. This dissolved in 60 cc hot alc got solid in 6 hrs standing giving porous white XXlle. Filter off wash well getting 26.2 grs salt, dried eq. which melts with off. from 120°-130°. Body is diff. sol. in methyl alc. and comes out as a gum; best dissolve in vol (= 100%) alcohol and got thus from the 26.2 grs salt 12 grs porous white salt which melts 100-110° & effers 116-118°. Tried to get from the 12 grs salt by Bux₂ etc a XX saccharin but got only 3.4 grs gum which was finally converted into Ca salt & by Kul etc got 2.9 grs an dry Ca salt combine with other comp. Ca salts (see below) and analyze. The orig alc. filt. from crop I gave on conc more of a granular salt crop II 17.85 grs, which gum with

BaO₂H₂ etc 10.75 grs Buene + 4.25 grs gum; gum with CaO₃ etc K₂C₂O₄ gum 3.25 grs air
 dry Ca salts (combine with cornp lot crop I see above), mother liquor from crops I + II (boiled with
 BaO₂H₂ etc gum 16.4 grs Buene and 8.45 grs gum + this with CaO₃ etc gum 8 grs Ca salt air (18 lbs)
 combine with 2 cornp lots Ca salts above & analyzed [i.e. 3.25 gr + 8. + 2.9 grs] ∴ total 14.15 grs
 got 8.83 % Ca; theory for 2nd body = 9.2%. Now convert rest of Ca salt to free saccharin by
 oxalic etc & got 9.6 grs gum. This was converted by 19.5 grs Buene into 30.7 grs salt.
 See xx this from 50 cc alcohol got 5.23 grams, crop I, of xx nodules of ^{Buene} *β*-meta saccharinate
 with dept 120°-125° or after rexx ^{this} gum 3.8 grs with dept 120-135°. The alc. fct. from crop I
 gum mashing more alcohol 6.48 grs more of same salt crop II dept 110°-125°.

Note; *β*-meta saccharinate of Buene nodules in 3 parts but about alcohol but comes out in great part
 according as a gum which subsequently gets solid on scratching; best use a small amt. of water, when it
 comes out directly in xx lls (nodules).

Now look crops I + II, 11.71 grs, + the 13.35 grs cornp. Buene salt obtained from Part I (see below) and
 convert by BaO₂H₂ etc into 15.3 grs Buene and 7.3 grs free *β*-meta saccharin; this is a gum
 which doesn't xx but gives a xx plangly by residue (see later); the gum dissolves with difficulty
 in acetic ether 7.3 grs taken & used 35 cc acetic ether ^{other} ^{gum} all but 2.1 grs dissolved but the
 acetic ether solutions give no xx lls ^{but a gum} in standing in air. for one week ^{at 143°-4}

I. Part sol in acetic ether 28.6 grs; gum in xx lls in dissolving in sun. not acetone ∴ real gum with
 85 cc acetic anhydride 7 lbs 100-110° and 9 lbs 120-5° & got 41.6 grs acylated gum which ^{precip} all
 dissolved in cold ether; now shake this ethereal solution with a sol of 15 grs K₂CO₃ in 150 cc
 H₂O & got 29 grs neutral acylated gum. The K₂CO₃ solution (beats) K₂O for 5 hrs add 22.5 grs 35% K₂O
 etc gum in ex to salt mixture with alc etc 6.8 grs gum; this is a mixture of saccharins & r. lactic as
 proved by heating gum with 20 cc acetic anhydride for 13 hrs at 100-120° & got 9.6 grs acylated gum,
 whole dissolved, except 14 grs tar + KCl in cold ether. On washing ethereal solution with
 10 grs K₂CO₃ in 100 cc H₂O got 4.5 grs neutral acylated gum (dis. car). The K₂CO₃ solution gum
 with HCl & hydrolyzed etc gum 3.5 grs gum which is in neutral sol in cold ether & ethereal sol. worked
 up with H₂O & K₂CO₃ etc gave only 1.75 grs Zn lactate 3rd xx lls 6.3.
 The 29 grs neutral acylated gum hydrolyzed 3x by 5 grs H₂O (plus 100°) gave 17.1987 grs Ca salt (an dry 24 hrs)
 which don't xx alone or with alc present ∴ convert by CaO₃ etc into 17.1987 grs Ca salt by oxalic to
 analysis: Ca = 8.99%. theory for 2nd body = 9.2% Ca. Now convert rest of Ca salt by oxalic to
 free saccharin & got 13.1 grs gum. This with 26.75 grs Buene etc gum 41.8 grs Buene salts.
 on dissolving here in 50 cc hot absol alc got 13.35 grs heavy gum. xx lls of *β*-meta saccharinate
 of Buene with dept 135-80 ∴ combine ^{crops} this with cornp lots from Part II (see above).
 The alc. mother liquors from Part I, II crops I + II in conc gum I crop II 3.75, II crop III 7.25 grs
 Buene salts with dept 100-125° ∴ combine these 11 grs strat with K₂O etc & got 6.8 grs Buene and 4.2 grs
 saccharin (alc. ext.) This digested 3x R₂ with 20 cc acetic ether all dissolved, except 0.7 grs gum + KCl,
 and the acetic ether extracts gum on cooling xx of *β*-meta saccharin 0.45 grs mpt 140-4°.

The alc. mother liquors from crops II + III (Part II + III) on conc etc gum 33.1 grs Buene salts (Buene
 these converted by 2 mls K₂O etc into 18.15 grs Buene and 11.2 grs saccharin (alc. ext.)
 on digesting latter 4x with 20 cc acetic ether R₂ found remain
 when dissolved and in

The University of Chicago

conc. the acetic ether solutions got xx of metasaccharin.
 The acetic ether solutions from Part II i.e. 7.3 g free β metasaccharin gum spread by xx
 from 0.45 g α metasaccharin mpt 144° now found to contain 5.8 g gum; were combined with
 corresponding acetic ether solutions from crops III Part II and crop II Part I (11 g gum) these
 had been freed from α metasaccharin (0.45 g). Det wt gums sol in acetic ether and found
 amt = 7.5 g Bu.B. v. v. This gum was now digested 9x with about 200 cc ether R.F. and
 found 3.8 g dissolved; 3.7 g insoluble; the latter was now digested 2x with 200 cc acetic
 ether R.F. and found all but 0.2 g (discarded) dissolved and these solutions vol. about 500 cc
 let stand in c.p. 2 days when got a sep. of 0.35 g gum only (discarded); 3.15 g β metasaccharin in
 the acetic ether.

The 11.2 g crude saccharins obt. from just soluble Bu.B. in c.p. I & II (see bottom
 p. 48) left only 1.7 g und. gum + KCl after 4th digestion with acetic ether (250 cc). On cooling
 these solutions on cooling gave 0.7 g metasaccharin mpt 140-4° (und. c. cold ale). Now det. amt
 gum left in solution and got 7.9 g Bu.B. v. v. This was digested R.F. 9x with 200 cc ether
 and found 4.95 g dissolved. The part insoluble in ether was found to dissolve on 1 digestion
 with 200 cc acetic ether i.e. 2.7 g or all but 0.25 g or on 2nd digestion all but 0.1 g found
 the acetic ether solutions allowed to stand 2 days in c.p. gave only 0.2 g und. gum; 2.75 g
 in solution.

Ether Extracts 4.95 g + 3.8 g see above, must exist mainly of cis and trans parasaccharin.
 The 4.95 g on shaking 7x with cold ether 3.8 g dissolved, tried to convert this 3.8 g by 16 cc H₂O 196
 and 1 g red p. S.T. Kek 11 hrs into 1 g acetyl butyrolactone spot making H₂O, ex. ether, wash w/ cold ale a fair amt
 of neutral lactone containing 1 g which does not volatilize with steam which on treatment with zinc dust ale
 gave only a small amt of α ethyl butyrolactone. (Note method or w/ lactone was destroyed by steam treatment.
 The other ether extract 3.8 g on shaking 7x with cold ether left 2.4 g und. and 1.7 g dissolved.
 Both these portions 2.4 g + 1.7 g were treated with H₂O & p (11 hrs w/o) & got fair amt neutral indolactone
 made in H₂O but on treatment with zinc dust and alcohol etc. gave very little lactones.

1st acetic ether extract now det. amt in solution Bu.B. v. v. = 2.5 g; convert this by
 5.2 g Bu.B. into 7.4 g Bu.B. salts; this xx from 3.5 cc H₂O and 45 cc alcohol gave on standing
 2 weeks in c.p. 2 g of Bu.B. saccharinate of Bu.B. mpt 120°-135° & Dept 138°-40° after drying H₂O & vac
 the ale. fli. crop. on indicator gave a gum which on drying H₂O in vac. got solid after pouring
 had 5.12 g salt with mpt. 80-100°; put this in a flask & shake with 40 cc alcohol when salt got all at once &
 much of it dissolves; decant & wash with 200 cc more ale & shake when part all dissolves
 this is obviously a salt of a new saccharin (saccharin? a sugar?).
 Acetic ether extract; the 3.15 g saccharin was converted by 6.2 g Bu.B. into 9.2 g Bu.B. salt.
 where xx from 6 cc H₂O and 55 cc alcohol in c.p. for 5 days. got 3.6 g β metasaccharinate
 of Bu.B. with mpt & Dept 130-135°; these in xx from 20 cc H₂O and 120 cc ale gave at once
 a large amount in a few hours. got 3 g + (crop I) with
 mpt & Dept 135-138° [Keep]

The ole filtr from 3.6 grs crop I, dest off Bu & one. gave 5.7 grs Bu & cin salt; this was dissolved in 15 cc spirit and on standing etc. 15 days got 2 grs more β metasaccharinate of Bu & cin with up to 100 grs 125-138 after drying (heavy vac) crop II. Now took the various crops of β metasacch. Bu & cin is. crop Ia + crop II + corresp. crop, 23, from the acetic ether solution (see above) & convert these 7.1 grs into Bu & cin 4.4 grs and β metasaccharin 1.5 grs ($2 \times$ acetic ether); the latter on standing gave 0.18 grs more $\alpha \alpha$ of meta saccharin up to 120-140°. The β metasaccharin left was a gum & was used up in an expt with H₂O & P. 100° 11 hrs which was not satisfactory as far as getting lactone was concerned but got a fair amt. To restore neutral to soda. The ole. filtr from crop II above now crop a red. gum left, got solid over H₂O in vacuo was powdered. got 2.32 grs [100%] β metasaccharin which gets only 5.12 grs on standing for most part, combine with corresp. lot above from 1st acetic ether extract & treat these with KOH etc & got 4.2 grs Bu & cin and 1.85 grs saccharin gum (acetic ether). The saccharin thus obtained was divided into 2 parts 10% strychnin salt 2% forcinchin salt but got a gum in 1st case, and also in 2nd case $\therefore$ u.g. 1% it is even doubtful if body obtained is a saccharin; ~~any~~ should say from above and also from next expt. with d. galactose & Nov 1570 that cis + trans para saccharin + β and α metasaccharin are only saccharins.

Nov 1705 Jan 6 + 26 '06 Feb 20 + 26 '06
90° Galactose and 15% NaOH. Took 100 grs galactose, 148 grs NaOH 50% H₂O and heat in st. 48 hrs from 40°-60°. Add 385 grs 35% HCl & take up mixture in ale etc & got 78 grs gum; on digesting this 5X with 600 cc acetic ether got 42.2 grs soluble and $\therefore$ 35.8 grs insoluble gum. The soluble gum was heated in -130° for 7 hrs with 120 cc acetic anhydride etc & got 64 grs acylated gum which heated again for 6 hrs 100-130° with 120 cc acetic anhydride gave 67.9 grs acylated gum. This dissolved except 5-10 grs brown tar in 1 1/2 cold ether and on washing this solution with sol of 20 grs K₂CO₃ in 200 cc H₂O lead left in ether 48.2 grs neutral acylated gum. The 35.8 grs insol. gum heated 10 hrs 100 with 120 cc acetic anhydride gave 62.5 grs acylated gum. This heated again with 600 cc acetic anhydride for 5 1/2 hrs at 100-100° gave 62.5 grs acylated gum. On taking this up K₂CO₃ in ether had left 27.5 grs insol tar (dis carded); the ether solution was now washed with same K₂CO₃ used above and freed 28 grs neutral gum left in ether which with 48.2 grs above makes a total of 76.2 grs neutral acylated gums. 46.6 grs saccharin gums. hydrolyzed 3X 7 hrs each 100° with 5 grs H₂O and got at end 6.8 grs gum which the K₂CO₃ solution used above was treated with 30 grs 35% HCl etc & got (f.e. ext) 6.8 grs gum which heated Bu & cin with CaO etc. gave 6.65 grs Ca salt & dec 3 days H₂O in vacuo; analysis Ca = 11.85% Now convert the Ca salt by theory $\therefore$ value to 4 grs gum, this is obviously a mixture of saccharins with sum of α & β lact. & acid present.

This gum was converted by 15 grs CaO₃ etc K₂CO₃ into 53.6 grs (and dry 64 grs) Ca salts. Ca det gave 9.6 % Ca; now convert rest of salt into 35.6 grs saccharin gums (by oxalic) and on digesting these 4X K₂CO₃ with 300 cc acetic ether found 30.1 grs had dissolved, and on cooling got a separation of 6.1 grs meta saccharin & the rest 135-140°; this $\alpha \alpha$ from 100 cc alcohol gave 4.85 grs of " " up to 144.5 + 0.5 grs in conc ale sol.

acetic ether extract, continued see p 51; on xx of the 12.15 grs crop I got finally 6.6 grs cp.
 B metasaccharinate of Buein with dept 137-8°; this with KOH alc gave 4.25 grs Buein and
 1.9 grs B metasaccharin (acetic ether ext 1x) as a gum which could not be got solid in any
 way (wed sun into alc & acetic ether & drying etc); treat the gum with 6 grs phenylhydrazine
 at 100-110° for 4 hrs (too long) and added ether etc when got a xx solid at once - 2.9 grs up to 85-90°
 this hydrazide is very hard to get pure; it comes out from hot acetic ether as an oil and from
 m. and also hot (much less) in opaque grouped needles up to 92-6° (xx 2x); 1st time took 2.5 grs
 in 10 cc alc got 1.2 grs up to 92-6° and on xx 1.2 grs from 7 cc alc alcohol got 0.6 grs up to 92-6° [keep].
 This is obviously the phenylhydrazide of B metasaccharine but found on crop alc. filter that
 got brown gums only (do do acetic ether solutions). Probably will work better next time
 if heat 90° for 1 hr with ph. hydrazine & then try other solvents for purif of emul by drying.
 ? wash by drying, after ppt by ether, with cold alc till snow white!?!
 The alcoholic filtrates from crop I 12.15 grs B metasacch. Buein ~~and~~ contained still 26.7 grs
 Buein salts as det Buein verno. On xx this from 5 cc Hro and 26 cc alc got a new crop of
 Buein body crops II, 8.45 grs up to 110-130° after drying Hro in vacuo.
 Now collect all alc. sol. feed from Buein body and det and Buein salts (about 25 grs) & treat
 with 2 KOH alc got 15.15 grs Buein and 5.30 grs saccharin gums (3x acetic ether), this
 was digested 4x R.F. by 200 cc ether and found 1.4 grs dissolved (gummy em. cont metasaccharin xx)
 The insol. portion contains 3.9 g saccharin from which got by sun. and alc etc in C.R. 0.15 grs
 in 300 cc acetic ether other sol. was allowed to stand in R.R. for 3 days; decant from lower gum sep out
 and found 2.9 grs gum left in the acetic ether Buein verno. This gum with 6.1 grs Buein etc
 8.8 grs Buein salts which dissolved in 2 cc Hro & 30 cc alc that stand 2 weeks in C.R. gave
 3.9 grs more B metasaccharin Buein with up to 120-138° (after Hro in vac). Now evap. not a
 salt on radiator spot 4.4 grs with up to 80-110° after pouring & drying Hro in vacuo.
 this salt ~~water~~ which is quite sol. in alcohol, gum with 2 KOH alc 2.8 grs Buein and 0.8 grs
 saccharin (1x acetic ether) (!) a new saccharin. Impossible.
 Oxidation of trans para saccharin by HNO₃. Took the 4.2 grs trans para saccharin from work
 sugar (see p 42 No 70) and dissolved it in 13 cc conc cp. HNO₃ (lab. var) and heated 45-57° for 19 1/4
 hrs (2 periods). At first got much brown fumes but in last 8 hours little. Now distill off HNO₃ at 15
 - 20 mm & heat finally Buein for 1 hr. Residue in diffent xx of oxalic & weighed 3.8 grs - i.e. dissol
 in 1/2 L Hro & heat Buein with 4 grs powd CaO₃ for 1 hr. Had 3.55 grs insol salt was digested R.F. 3 hrs in bath 100-110° & filter
 filter to small volume of sol. The 3.55 grs insol salt left 1.85 grs insol CaO₃ & CaO₄ and evap. aq.
 left leaving 3.3 grs insol. salt still with acetic etc left 0.2 grs (discarded). The aqueous filtr in conc to about
 conc on WB gave xxle can't be more than 0.2 grs (discarded). The aqueous filtr in conc to about
 30 cc gave 0.4 grs xx Ca salt which dissolved in boiling in 150 cc Hro & on cooling little comes
 out but on crop on WB got flat glistening scales not well defined but perfectly
 brown & viscous [keep] (!) is it corn
 ? by again using more dil HNO₃ etc & cp. No 27
 contains much gummy Ca salt
 (!) much trans para saccharin

The University of Chicago

92°

Bucium salt of α metasaccharin. 1g metasaccharin (mp 144-50) and 2.43g Bucium etc gave

3.4g salt; the salt comes out as a gum on diss. in 15cc absolute alcohol & this gets solid slowly giving 2.6g mp 148-55° & depts 158°; when dried H_2SO_4 vac 107 = 2.4g shows m.p. 152 thus depts 153° on xx this salt 2.4g from 1.5cc H_2O and 12 cc alc. f.p. xx to sep out rapidly after 3 days got 2.2g translucent flat needles (groups of tens) which decompose after drying H_2SO_4 vac from 123-133°

93°

Properties of α metasaccharin. 1.6g dissolved R.F. in smallest possible amount of acetone

Took 100 cc and on standing 24 hrs in C.R. got 0.9g flat needles mp 144-50. 1.6g α metasaccharin took 350 cc acetone ether to dissolve R.F. and on cooling & finally getting stand 1 day in C.R. got 1.3g xx lvs to separate out.

94°

Phenylhydrazide of α metasaccharin. Took 1g metasaccharin and 3g phenylhydrazine and heated

for 2 hours 120-140° in oil bath, add ether etc. and got 1.75g crude solid. This digested R.F. with 200 cc acetone ether left 0.3g xx needles which melt from 113-15° and on cooling filtrate got 0.8g flakey substance mp 108-112° (another liquor gave a gum: discarded). Continue 0.8g + 0.3g xx from 200 cc alcohol + got 1.1g xx flakey which melt after drying H_2SO_4 in vac from 108-115° [? some unchanged metasaccharin present] took 1.1g and heated it 14 hrs at 130-140° with 3g phenylhydrazine etc, got 1g crude product mp 105-110° which xx from 20 cc alc gave 0.8g xx flakes mp 105-90° (dried H_2SO_4 vac) from 113-115° (ready for analysis). Cf Kiliani Sarsla Ber 26 1649

95°

Glycerinic acid + H.J. 2g glycerinate of la 2Hro mp 1350 + 10 cc H.J. 196 heated st. took 5 hrs and

H_2O , ext. 3x by ether then ext 3x with 30 cc H_2O and soda to soda sol. 1x fresh ether then acidify with c. dil H_2SO_4 & ext 3x by ether & dry each - gave 20.8g crude β or γ glycerinic acid (dried H_2SO_4 20 hrs) mp 74-81°. This was xx from 18 cc hot ligum (70-80°) got 1.8g xx flakey (dried H_2SO_4 vac) mp 80-83°; mother liquor crops about 0.2g more just as pure: D.K.

96°

Props. of cp. r. glycerinic acid. took 18.5g gum which was digested R.F. shaking 3-4x with 400 cc ether

off H_2O BuB in vacuo 18.5g 3 shakes dissolved 2.3g; 2nd digestion 2 hrs 4 shakes dissolved 1.9g; 1st time and soluble in ether. Took 54.6g xx Ca glycerinate 2Hro mp 134° & treat with 24.05g oxalic 2Hro etc got 39g r. glycerinic acid BuB vacuo: on heating this R.F. with 500 cc acetone ether 28g dissolved 1st time and 6g 2nd time, leaving 5g CaC_2O_4 + gum (discarded). The acetone ether extracts distilled off gave 34.1g r. glycerinic BuB vacuo. Made this in H_2O solution up to 170 cc: 1g r. glyc. in 5cc sol. Took 25cc of this 20% glyc. sol & got with $CaCO_3$ etc 6.04g cp. r. glycerinic 2Hro. Bucium salt (cf. No 17) took 50.8 cc of 20% glyc. serum by 33.65g Bucium (theory 37.1g for 10g) into salt got 42.3g. This dissolved R.F. in 150 cc alcohol gave on cooling heavy transp mass xx lvs 9.8g depts 220° (no loss on drying in vacuo). The alc. filtr. in conc. gave 2.5g in C.R. gave 24.45g more which had depts 210° alc. filtr. in conc. gave 2.5g crop IV (keep).

97) H₂O on saccharin and on iso- and meta-saccharin. 2g meta-saccharin 9cc H₂O 1.96 and 0.5g P
in ST. 60° for 11 hours, gave much oil when H₂O is added, etc. other wash soda & got a neutral oil cont. In
which with zinc dust & alcohol gave very little lactone [? heat higher].
a similar expt with 1.25g iso-saccharin 6cc H₂O 1.96 + 0.3g P gave with H₂O on ice of an oil heavier than
H₂O but on breaking this with zinc dust & alc gave traces of lactone only.
Took 3g saccharin 0.7g P and 12cc H₂O 1.96 heat ST. 7½ hrs 60° & got a neutral oil in lactone
from which by zinc dust & alc got 0.8g of dimethyl butyrolactone bpt 199° - 201°, little soluble in
cold H₂O - method is not quant. heat higher. see below also
soln of 40g d. glucose (48-9°) in 80cc H₂O this a sep. funnel slowly
165cc H₂O. The NaOH sol was in a d.f.

from which by zinc dust &ale got 0.5g. see below also
Cold H₂O - method is not great. Heat higher.
(980) d. glucose & 33% NaOH. Add a solution of 40g d. glucose (148-9°) in 80cc H₂O this sep. funnel slowly
to a sol. of 100g NaOH (97.7%, det by titr) in 165cc H₂O. The NaOH sol was in ad. f.
(mixing approx 5c. 15cc H₂O) to a sol. of 100g NaOH (97.7%, det by titr) in 165cc H₂O. The NaOH sol was in ad. f.
terminated by condense with a receiver & agitator & the lamp of sol. when sugar added was 60° & it rose
to 72° then heat of reaction making aq. sugar (took 15 minutes). Now raise temp of bath to 100°-108° and
keep then for 2 1/4 hrs (temp inside was 93-97° during this time). The alk. sol at end is wine red in
color and no absorption of air or evap. of gas took place. Now add H₂O and 266g tit & 33.5% HCl etc
distilling off in vials Buns. The ^{total} eq. dist. took only 13cc & NaOH to make alkaline (roughly done)
is only 0.5g - 0.6g HCO₂H was found in reaction. The salt residue (2 lots) was digested 2x in
cold with 700cc ether 1x R.F. and found that 24.8g gum dissolved; this was now dissolved in 400cc
cold ether & sol decanted from sun. and insol gum (put with acetic ether extract) and the ethereal
solution evap & treated with 20g ZnCO₃ & H₂O etc gum 26.58g in lact 3hrs; crop I, ^{gummy} = 12.38g; crop II = 7.4g
crop III = 4.2g crop IV, ^{sticky} = 2.6g. The eq. felt from crop II contained about 8.55g zinc salts
of cis trans panto saccharin (discarded). ^{5 of am 335, 326} This corresponds to 16g 2. lactic acid!!
Now digest salt residue (in 2 lots) R.F. with 700cc acetic ether 3x and found residue weighs 145g (theory
NaCl = 142.9g). Dist wt gums in acetic ether and got 8.25g (ent xx of saccharin)
This gum (8.25g) was treated with 33cc H₂O 1.96 and 2g P on Buns. for 14 hrs (S.T.) and H₂O got
much oil, exto c. ether & wash c. soda etc. Got only a small amt of neutral in lactones which
with zinc dust &ale gave too small an amt. of alkylated butyrolactone to handle. V. ||||
The soda solutions exto c. fresh ether & then acidified with dil H₂SO₄ gave much heavy oil ||||
which on treatment with zinc dust &ale etc. gave 2g or more oil still containing iodine: not satisfactory
? best to heat in S.T. 130° - 140° to get more complete action
with 98° using d. galactose inst of d. glucose & modify by heating
165 (5 minutes) & then treated

The soda solutions which on treatment with zinc dust take etc. gave
? but to heat in S.T. 120° - 140° to get more sample

99° d. galactose + 33% NaOH; repeat expt. 98 using d. galactose inst. of d. glucose & modify by heating temp of NaOH sol. at 80° at beginning of expt; temp rose to 92° as sugar is added (15 minutes) when heated 2½ hrs longer in bath 100-108° (temp inside 92-80). Redd Hno + 26.6g 33.5% tetr. HCl etc. The aq. dust gave a decided test for HCl in this case and found it took 17cc NaOH solution 100% test to make alkaline (sol. for yellow, ^{when alk. present} ~~acetol present~~). The salt residue (2 lts) shook 3x in cold each with 700cc ether and found 22.5gms gum dissolved (Burr one). This with ZnCO₃ etc gave a total of 13.3gms Zn lact 34ro [comp to 8.0465gms v. lactic acid [cf ann. 335 + No 27 when got only 2.7g Zn lact 34ro] comp I, 9.5gms comp II 3.8gms sticky; the aq. filly comp II gave 23gms gummy zinc salts of cis & trans para saccharin which were heated in S.T. 100° for 10 hrs with 92cc. H₂O, 96 and 4gms P; add Hno etc to c ether swash c. soda etc. got similar results as in 98% u. (i.e. not satisfactory)

The University of Chicago

The salt residue was now taken up 3x by ^{400cc} acetic ether R. F. solvent of acetic ether got xx of meta saccharin, 1.8 grs mpt 142-4°; and got also 6.2 grs gums. salt residue weighs 140.7 grs heavy 142.9 grs ∴ must have made a slight mistake in weighing out NaOH used ∴ excess of HCl noticed is also explained.

Conclude from 98° + 99° + expts with 15% NaOH on saccharose dextrose cum 335 326 etc that the v. lactic acid is formed from a splitting of the 3 ketol groups ^{into glycerine & glycolic} acid is formed and that the other reaction products are C6 saccharins which are 2 mols which goes by shifting of OH to CH₃CO-CHO etc. It is certain that the v. glycerinic chief product is case the NaOH is 7½ % with dextrose laevulose and when NaOH is 15% with d. galactose. [? better use BuOH in future expts.]

[?] there may be some glycerinic traces; test for this later with great care

100° d. glucenic acid, BuOH salt, phenylhydrazide etc. took 5 grs CaF₂ K₂ gluconic (about 50%) and added BuOH tell just neutral eq. sol. (look 58.5 grs). got 8.4 grs salt BuOH mero. This described in 8 cc H₂O + 80 cc hot alcohol gave a grad. sep in large amt of opaque heavy prisms (1 day at. + 1 day c.R.)

Salt melts from 120°-125° with efferv. but after drying 24 hrs at 100° in vacuum it decomposes from 150°-155° got 7.34 grs anhyd. salt ∴ sep is quite complete. This salt with 2 mols KOH + HCl etc gave 4.75 grs BuOH mero and 2.8 grs d. glucenic (do. do. aceline). It dissolves at once R. F. in 50 cc alcohol leaving depositum with 200 cc acetic ether (do. do. aceline). It dissolves at once R. F. in 50 cc alcohol leaving 0.4 grs after long depression with 200 cc acetic ether. Took 2.6 grs of this gum and mix with 7.8 grs phenylhydrazine mpt 170-175°. This xx from 0.2 grs K₂CO₃ + gum. Took 2.6 grs of this gum and mix with 7.8 grs phenylhydrazine mpt 170-175°. This xx from

Mass soon gets solid, add ether etc got 2.8 grs crude hydrazide mpt 190-200° ∴ d. glucenic ph. hydrazide (cf E. Fischer). The body is very diff. soluble in boiling alcohol, acetic ether, acetone but quite soluble in 7-8 pts boiling water and comes out slowly not completely on cooling in opaque nodules (Keep). It is diff. sol in boiling CH₃OH, insol in C₆H₆ and dissolves slightly in amyl alcohol on cooling. It is diff. sol in boiling CH₃OH, insol in C₆H₆ and dissolves slightly in amyl alcohol on cooling.

3°) Ca salt d. glucenic; made from 10 gr 50% acid etc same to 25 cc gives Ca salt in opaque fine needles m. 678°C

4°) The phenylhydrazide is better made acc to 2° than acc. to Fischer's method in the sol. with ph. hydrazide

5°) Took 40 cc of CaF₂ K₂ 50% acid & took off the BuOH mero got 21.6 grs gum (a mixture of anhydrides) dissolved each time and under bell of solvent got from this 2.8 grs gum. 6°) Took 40 cc of CaF₂ K₂ 50% acid & took off the BuOH mero got 21.6 grs gum (a mixture of anhydrides) dissolved each time and under bell of solvent got from this 2.8 grs gum. 7°) Took 40 cc of CaF₂ K₂ 50% acid & took off the BuOH mero got 21.6 grs gum (a mixture of anhydrides) dissolved each time and under bell of solvent got from this 2.8 grs gum.

8°) Took another 10 cc of CaF₂ K₂ 50% acid & took off the BuOH mero got 21.6 grs gum (a mixture of anhydrides) dissolved each time and under bell of solvent got from this 2.8 grs gum. 9°) Took 40 cc of CaF₂ K₂ 50% acid & took off the BuOH mero got 21.6 grs gum (a mixture of anhydrides) dissolved each time and under bell of solvent got from this 2.8 grs gum. 10°) Took 40 cc of CaF₂ K₂ 50% acid & took off the BuOH mero got 21.6 grs gum (a mixture of anhydrides) dissolved each time and under bell of solvent got from this 2.8 grs gum.

70 Took 2g ca 7K gluconic chloride of H₂O Bunsen's strait gum left 1.4 gms with 3cc phenyl hyd at 100° for 1 hr then add sun. amt hot alcohol & stir & cool & add ether. got 2.1 gms phenyl hyd & 2.1 gms with dept 195-60°. This xx from 19cc H₂O gave 1.66 d gluconic ph. hyd dept 200°: O.K.

80 Took 2cc 50% d. gluconic (ca 7K) + 3cc ph. hyd + 5cc alc and heat mixture to 80° for 1 hour. the hydrazide comes out rapidly after 10 minutes and on cooling got large amt of white flat needles: add ether (if necessary) and filter & got 1.6 gms ph. hydrazide dept 195-60° or xx this from 15cc hot H₂O got 1.25 gms shiny flakes had the dept 200°.

90 Took the 9.65 gms cinchonin salt of d. gluconic acid (see No 23) made Dec 20, 04 & dissolved in 10cc H₂O & 10cc hot alcohol; on 24 hrs standing got 4.9 gms air dry cp. salt leaving dept 180-185°; mother liquor evap on w.b. gave again much got solid on heating this with cold absol. alcohol got 2.1 gms more salt with dept 175-180°. Made a new lot of cinchonin salt 13.7 gms and xx this from 10cc H₂O & 10cc cold alc gave 1.1 gms more salt with dept 175-180°. It is probable that some d. gluconic cinchonin was present as d. gluconic ca 7K was found to contain it see above. (mg. see p 53)

100 Preparation of trioxysuccinic acid (see No 17. (of Oct 31904). 50 gms Tartaric acid in 20cc H₂O, added to sol of 18.78 gms H₂O in 10cc H₂O + 1.2 gms NaK tart. in 10cc H₂O & more 10cc H₂O in all. Cool in 9. m. & add 320cc 3.5% H₂O₂ in 80 minutes temp > 70°; let stand 2 hrs in ice H₂O & then add 38cc fuming H₂SO₄ (made from 2 vols ca 7K fuming + 1 vol conc cp. H₂SO₄). Got 6.95 gms xx after 3 days & 5 cc brx when add 38cc more fuming H₂SO₄ for standing 4 days ice brx got 4.67 gms xx & after 7 days standing 10.5 gms xx: total of 12.67 gms trioxysuccinic. Expt II using 2x amt of reagents & mixed in 2x the time & got 13.65 g + 10.4 + 2.25 gms or 26.38 gms from 100 g tart. Expt III gave 19.65 gms. Expt IV (like II & III) gave total of 22.95 gms trioxysuccinic acid. (see April 24-May 7, 06)

102 Quant. conv. of trioxysuccinic into glycolaldehyde (see No 2). Took 3.95 gms trioxysuccinic (made Oct 28 1904) and dissolved it in 10cc H₂O and heat in bath 65-75° for 1 1/2 hr and then finally on Bunsen; lead for fire air drawing this solution in a flask connected with a water condenser and then with 2 cylinders 22.5 gms BaO₂ & 8 H₂O in 45cc H₂O in 1st cylinder and 13.5 gms BaO₂ & 8 H₂O in 270cc H₂O in 2nd cylinder. began 10:35 at 65° and at 11:15 am sol. is boiling & stopped at 11:45 am: total time 70 minutes. Got 8.5 gms BaO₂ dissolved 100° there is 9.375 gms BaO₂ is conv. is just quant (of Oct 22 04) & O.K. (if wise may condense)

103 Glycolaldehyde, CuO₂H₂ + NaOH. Took 13.95 gms trioxysuccinic acid (13.833 gms comp to 5 gms glycolaldehyde) and heated with 2 1/2 pts H₂O at 60-65° and then finally for 1 hr on Bunsen (the glycolaldehyde, used in No 102, was included in this). Now prepare a hot mixture of 38.25 gms CuSO₄ & 5 H₂O (B + A), 5 mols, in 203cc H₂O and then add a sol. of 16.78 gms NaOH (97.7% titr) in 68.8 gms H₂O and shake; then add quickly the aq. sol. of glycolaldehyde (5 of A) & shake; reduction takes place at once: heat on Bunsen and add gradually the rest (27) of the glycolaldehyde solution & boil 1 hr on Bunsen, filter & pour solution is brown & entirely free from Cu. N.B. there was probably an excess of glycolaldehyde as much Cu used comp to 2 1/2 atoms SO for 3 mols Cu₂H₂O₂ taken; the latter must take up at least 30 as some H₂CO₂ is formed in expt.

cf. expt with glycol ~~NaOH~~ (57) 46) where glycolic is main product

The University of Chicago

(adding the distill of 12th time)

filter and add 10.3 grs 33.5% (titr) HCl when distill off H₂O etc BoB in vacuum
 the aq. dist (cont no HCl) was made up to 1L. 7.64cc $\frac{n}{10}$ NaOH were required to
 neutralize 100cc of distillate (phenolph) $\therefore$ amt HCO₂H total present is 0.3514 grs.
 100cc of distillate treated with soda + 30.57 g $\frac{n}{10}$ KMnO₄ $\frac{1}{2}$ hr at 60° and then acidify
 with HNO₃ and add 20cc $\frac{n}{5}$ oxalic + dilute back with 23.51cc $\frac{n}{10}$ KMnO₄. From this
 amt of HCO₂H present total = 0.3344 grs.
 Now take up solid residue in 100cc H₂O and add 2cc 35% HCl sppt. hot by aq. vol of
 alcohol (got 19.1 grs ^{and 18 hrs} NaCl + NaBO₂). Distill off H₂O etc from filter ~~stuck up~~ salt residue
 R.7 with alcohol when subsequently digest ale extracted with ether. This was treated
 got 7.2 grs more NaCl + NaBO₂ and found 3.7 grs gum in ether. This was treated
 with H₂O + CaCO₃ etc got 1.85 grs milk CaCO₃ + on cone brown felt to small volume
 got a total of 1.85 grs xx Ca " " and mother liquor contains a gummy very sol Ca salt
 got only 0.1 grs more xx Ca " " [air dry 2 days snow white]; aq. felt depositate K₂CO₃
 [? Ca succinate mixture] - (?) a portion of the glycolic salt was condensed this
leaving in this 1 hr at 80° $\therefore$ n.g. cf do do No 2.

104 d. glucose and aqueous K₂CO₃ or Naacetate. a solution of 200 grs K₂CO₃ in 200cc H₂O
 was treated with 40 grs d. glucose in 100cc H₂O. No rise in temp & now heated in a bath 100-110° (temp
 rose 94°-102°) for 6 hrs (cf 98° & 99° for app). Then is much sweetening & sol. is very dark brown
 at end but reduces Fehling's solution very decidedly $\therefore$ very incomplete reaction $\therefore$ n.g.
 II a similar expt. with 200 grs fixed Naacetate in 200cc H₂O and add 40 g d. glucose in 100cc
 H₂O at 85°-90° subseq. heat 100-110° bath for 29 hrs. sol. is very dark, much sweetening,
 has odor of acetic acid when hot but still reduces Fehling's sol. very strongly $\therefore$ n.g.

1050 Phenylhydrazine in glycollic & glyceric acid.
 a) 3 grs cp. glycollic acid and 6 grs phenylhydrazine are mixed and heated in a bath 100°; get salt formation
 at first and then a violent effervescence with formation of H₂O; on heating for 1 hr and add ether etc
 got an oily hydrazide insoluble in ether but very soluble in H₂O & cold alcohol. gets hot and meringy gets
 18 glycollic in 1cc absolute alcohol and add 2cc phenylhydrazine in 1cc absolute alcohol. gets hot and meringy gets
 6 sided plates $\rightarrow$ O,
 c) repeat b) but used 15cc alcohol on mixing reagents + 10cc ale. for rinsings: got 1.9 grs salt; it can be
 xx from absolute alcohol when melts from 100°-102° & effervesces 110°-115°.
 d) took 3g cp. glyceric acid gum (BoB vacuum) and 6cc ale and 6cc phenylhydrazine + 3cc absolute alcohol; got
 no separation of salt on standing in ice H₂O for 1 hr $\therefore$ add 12cc ether & scratch & got an oil but no xx etc.
 next day distilled off ether & ale in BoB & got a brown oil very sol. in ale & water & unsol. in
 ether. This enables one to separate glycollic + r. glyceric acid s.
? but also $\pm$ lactic acid (to sep. succinic from lactic).

106°

Laevulose, Cu²⁺ and NaOH; (cf No 9)

Took the 88 grs gum obtained (see No 9) and

unreleasable as acetic anhydride is 152

leached it with 264 cc acetic anhydride 9 hrs at 100°-110° and got 139.5 grs acylated gum or after digestion 4x R.F. with ether got 98.4 grs soluble gum and 41 grs insol acylated gum (discarded). The sol. acylated gum was washed in 1 1/2 l ether with 60 grs K₂CO₃ in 800 cc H₂O; got 33.5 grs neutral acylated gum which on hydrolysis 3x 5% H₂O 8 hrs each 100° gave 18 grs of C₄-C₅ acids; on digesting these 7x R.F. with 400 cc acetic ether found 12.9 grs dissolved and the rest except 0.6 gr (discarded) dissolved very easily R.F. in acetone. Now unite again what at R.F. was as 18.4 grs. treated these with CaCO₃ etc got 19.6 grs Ca salts air dry 18 hrs; powder these & dry 4 hrs at 80° and then 4 hrs at 100° got a loss of 1.5 grs H₂O; analysis for Ca gave 10.17 % Ca. Take out of salt & ppt Ca by oxalic etc got back 13.3 grs gum which with H₂O and 34 grs Buein gave 53.4 grs Buein salts. XX these from 200 cc H₂O and 120 cc alcohol and got crop I with dept 150° 7.5 grs ? d. arabinic of Buein, and then crop II 4 grs, dept 195°-197° proved to be mainly d. Mannonic Buein as got from this by XX 2.9 grs sp. d. Mannonic Buein & from this by KOH etc got 0.35 grs d. Mannonic lactone mpt 149-153°. The ale fell to crop II gave 5.9 grs salt with 2 cpts 140-150° ? d. arabinic Buein, but this subseq proved to contain 1.9 grs d. Mannonic Buein. The ale. filtrate from crops I & II gave 27.4 grs Buein salts which with 2 KOH etc gave 18.35 gr Buein and 7.7 grs acid gums (ale extn) & the latter, on digestion 3x with acetic ether 200 cc dissolved 3.2 gr + 0.8 gr + 0.6 gr = 4.6 grs in all [this must contain l. threonic & d. gluconic acids, for as the Buein salts made from it are mainly quite soluble in alcohol & gummy]. 35% HCl etc got 40.4 grs gum (ale extn) & after hydrolysis K₂CO₃ solution. on acidifying with theory 35% HCl etc got 40.4 grs gum (ale extn) & after hydrolysis 8 hrs 100° with 200 cc H₂O this became 33.4 grs gum (brown). On digesting this R.F. this with 500 cc ether found 3 grs gum dissolved & then with CaCO₃ etc gave 3.8418 grs Ca salt (air dry 24 hrs). On drying this 48 hrs H₂O in vacuo 8 1/2 hrs at 100-110° found loss of H₂O = 12.05%. Cadet. now gave 13.6 % Ca [i.e. body must be mainly glycerinic & C₄ acids]. The main gum left insol after 1x digestion with ether i.e. = 30.4 grs was now digested 3x with acetone and pressed all dissolved 1st time leaving only 4.7 grs insol KCl + gum (discarded). The 25.7 grs gum in the acetone was now converted into Ca salts pptd by alc air dry 18 hrs & got 34.2118 grs. On drying this 48 hrs H₂O in vacuo & then 8 1/2 hrs 100-110° found loss of H₂O = 9.2%. Ca in dry salt = 12.42 % } Ca for glycerinic 24% = 12.9 %
Ca " " C₄ " = 10.81 %
Ca for C₅ glycerinic 2 H₂O = 13.99 % } 100cc suspt 100° and got 0.5 grs crude only insol propionic acid. On taking 2 grs of above dry salt with H₂O 196 and got 0.5 grs crude only insol propionic acid. i.e. glycerinic must be present in it. The d. gluconic acid found in reaction probably was not extracted by the acetone orig used to get the 88 grs gum. Furthermore the C₄ C₅ and C₆ acids by treatment with acetic anhydride etc go into the K₂CO₃ solution in large amounts. Provided also in above expt that sp. d. Mannonic Buein when conv into Buein and free acid gums only about 1/2 to 3/4 d. Mannonic lactone & rest is a gummy mixture of various anhydrides which go back with Buein into sp. d. Mannonic Buein XX in above volum. weighs from H₂O sale.

see Anderson

[59]

The University of Chicago

107) d. galactose, $C_6H_{12}O_6$ and $NaOH$; [cf. Oct 4-10 '04 and Jan 9 and Feb 26 1906].
Took 56.4 grs d. galactose strated with Cu dry 5 Hro + $NaOH$ exactly as in case of d. glucose
in Ann 335, 331 & then add HCl etc. got 39 grs non volatile acids BuO_3 in extracting R.F.
with acetone. Rinsed this 10 1/2 hrs at 100-110° with 100 cc acetone (only dry it 6 3/4 hrs acetone gum.
putting this up in ether R.F. found only 8.4 grs acid acetone (hardly can). The ethereal solution
(was now washed with sol of 40 grs K_2CO_3 in 500 cc Hro. got 18.5 grs neutral acetone gum which on
3x hydrolysis 5 Hro 9 hrs 100° gave 9.8 grs C_4 C_5 C_6 gums. On digesting these 6x R.F. with 400 cc
acetic ether all but 3.6 grs dissolved & this easily went into acetone 1x except 0.4 gr (discarded).
Combine acetone & acetic ether ex. levels & let BuO_3 vapor as 9.7 grs. Convert this by CuO_3
etc into 10.35 grs Ca salt, air dry 18 hrs. Powder salt & dry it 4 hrs at 80° & 4 hrs at 90° & 100° &
found loss of Hro = 0.75 grs. analysis dry Ca salt = 9.78% Ca . Now convert Ca salt left by oxide
etc into 7 grs gum (brown, ale extr) and this gum with 16 grs Boucin 24.9 grs Boucin salts; on diss
here in 12 cc Hro and 60 cc hot ale got 5.2 grs crystall needles, crop I, which melts with efferv at 106-107°
or after drying Hro in vauo wt = 4.9 grs & sublimed now softens 115-120° & softens at 135° on xx this
from 4 cc Hro and 30 cc ale got heavy opaque xx needles 2.6 grs after drying Hro in vauo & on xx again
(? talonic Boucin). The ale filtr from crop I gave 20.3 grs Boucin salts BuO_3 vauo & on xx again
3 cc Hro and 15 cc alcohol got a new crop of xx like much like I = 7.1 grs; crop II. (? talonic Boucin).
Took crops I & II and converted these by 2KOH into 7 grs Boucin and 3.8 grs gum (ale extr).
The latter was heated 1 1/2 hrs with 9 grs phenylhydrazine at 100-110° & soon got solid. add ether
& stir as mass was sticky & alcohol and got thus 5.5 grs wool yellow powder; this xx
from in. and lost water gave 1.5 grs d. galactonic phenylhydrazide dect 200-205° or on xx again
got 0.9 grs dect ~~talonic~~ xx like [keep]. The ale. solution contains gummy hydrazide as
? of talonic l. xyloxyd. l. by xonic (?) acids.
The ale. filtr from crops I & II above contain only 9 grs Boucin salts. Discard at this point.
K₂CO₃ solution. acidified by HCl 60 grs 35% ale gave 20.2 grs gum (ale extr) & this by dry 2 1/2
hrs at 100° with 5 Hro gave 17.9 grs gum. On digesting this 3 Hro R.F. with 500 cc ether found only 0.5 grs
dissolved: can't be more than traces of glycollic acid in the gum. On digesting 3x R.F. with acetone
all but 3 g gum (discard) dissolved. Combine the acetone extracts & then convert into Ca salts
by K_2CO_3 ale etc. got 18.832 grs (air dry 18 hrs). This lost after drying 48 hrs Hro in vauo
1.235 g Hro on drying further 8 1/2 hrs 90-110° had total Hro = 1.6684 grs or 8.86%.
 Ca det in dry salt now gave 12.15% Ca . must be mainly C_3 & C_4 acids. Took 2 g of the
dry Ca salt and heated s.t. with 10 cc H₂O 196 for 5 hrs & add Hro ex. ether when cold etc and
got a small amt (not more than 0.2 g) of only β ion propionic acid.
108) d. glucose, $C_6H_{12}O_6$ & $NaOH$ [cf. March 7, March 22, April 13, April 22, 1906].
Took 56.4 grs d. glucose (purity 148-9%) in 280 cc Hro and add a sol. of 382.5 grs xx Cu dry 5 Hro (= 5 marks
or 2 1/2) in 2030 cc Hro & then add a sol. of 167.8 grs $NaOH$ 97.7% by titr. (163.8 grs or 13 and $NaOH$)
in 688 cc Hro. Warm, after shaking at once in a pan of Hro at 40° raise this to boiling as
quickly as possible. In 10 minutes after mixing had much CuO down
in 20 minutes sol. is still green but faint all
 CuO . Heat boiling Hro for

