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Now took rest of Ca salts, 3.4007 g and made up with H_2O so that $p = 4.0$ & found α in 1 dc tube was $-0°.54$ ∴ $[\alpha]^{20}_D = -13.6$. Now treat aq. sol. with 1.683 g oxalic $2H_2O$ & got 100° vacuo 2.65 g gum which contained xxlle. Found $[\alpha]^{20}_D$ of this as $-1°.88$ ($p = 4.0$) ∴ treat it with 7.4 g Chinin & got 5 hrs BzOH etc a total of 6.62 g diff sol (in H_2O) Chinin salts mpt 170–180° which with 5.0 g $Ba(OH)_2$ etc gave 5.2 g chinin & 1.15 g (alc ext) crude lactone acid full of xxlle. On ext. this R.F. with acetic ether (about 150 cc) & filtering from traces brown tar & Ba salts residue. filtrate in WB got 0.67 g xx prisms mpt 165° of α dextrometasaccharinic mono lactone acid, $C_6H_8O_6$ with $[\alpha]^{20}_D = -4°.73$, i.e. 0.6081 g subst and 14.7025 g H_2O ∴ $p = 3.97$ $d = 1.011$ at & found α in 1 dc tube $= -0°.19$. The aq. solution of 0.6081 subst now titrated using litmus. On adding about 45 cc $\frac{n}{10}$ NaOH the solution was permanently alkaline in cold (1 mol = 34.55 cc) & on warming thus got acid again ∴ obviously a lactone acid. add more alkali again & finally found permanent blue only after 69.1 ccm $\frac{n}{10}$ NaOH had been added (= theory). ~~the~~ addition of red litmus at this point showed no change in color ∴ pract. neutral solution. according to calculation must now have 0.8224 g $C_6H_8O_7Na_2$ in solution ∴ distill off H_2O in vacuo & make up gummy Na_2 salt with 20.4691 g H_2O to total weight 21.2915 g ∴ $p = 3.86$ and found α in 2 dc tube $= -2°.75$! ∴ $[\alpha]^{20}_D$ of $C_6H_8O_7Na_2 = -35°.22$. hence space formula of α dextrometasaccharinic acid must be

$$COOH-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-CH_2OH \qquad \text{Q.E.D.}$$

Now add 69.2 cc $\frac{n}{10}$ HCl to aq. solution & distill off in vacuo & acylate lactone acid & 2 mols NaCl left with 4 cc acetic anhydride 8 hrs 100–120° & got (cf. No 53) 0.18 g yellow β oxy muconic lactone xxlle mpt 228°.

<u>A second experiment</u> taking 14.53 g cp. Ca salt of α dextrometasaccharin & treating with 4.6 g oxalic $2H_2O$ etc gave <u>11.2</u> g crude $C_6H_{10}O_5$ which got entirely solid with xxlle. ditto another lot (upsorns?) 9.66 g c.p. Ca salt gave on similar treatment <u>7.4</u> g crude xx $C_6H_{10}O_5$. <u>Unite these</u> ∴ <u>18.6 g</u> & dissolved in 74.4 g HNO_3 (1.21 sp gr) & heated 60°–65° for 48 hrs & got (90° 25 mm) 15.9 g residue filled with oxalic xxlle. Digested this repeatedly R.F. with ethyl acetate until no more gum apparently dissolved & had left (by diff) 4.4 g insol brown tar, easily soluble in cold H_2O & on distilling off (100° 25 mm) got 4.1 g tar. This acylated for 8 hrs 100–120° with 13 cc Essigs. anhydride gave back (100° 25 mm) 4.4 g acylated tar & on extracting this R.F. with acetic ether etc (100° 25 mm) got 0.27 g 2-oxymuconic lactone mpt 228°. The acetic ether filtrates gave 12.1 g gum cont. xx of oxalic acid & these were now digested BzOH 2 hrs with 4.0 g powd CaO & got 4.4 g insol $CaC_2O_4 + 2H_2O$ & aq. filtrate digested for 6 hrs with 0.5 g powd CaO gave 0.86 g more insol CaC_2O_4. The aq. filtrate was now treated with 7.0 g oxalic $2H_2O$ so as to have a slight excess C_2O_4 & distill off in vacuo & got 8.0 g gum which digesting well R.F. with much ethyl acetate left 1.8 g insol tar & on dist off solvent got back <u>6.0 g</u> gum. This was now digested with 22.0 g Chinin (6 hrs BzOH) & all except 0.6 g (in H_2O) dissolved & on conc. aq. filtr etc got a total of 20.06 g (in 3 crops) of diff. sol. Chinin salts mpt 160–170° which treated with 15 g $Ba(OH)_2$ etc gave 16.37 g Chinin & <u>3.28 g gum full of</u> xxlle. These were resolved by dissolving in acetone & distilling off this solvent & adding small amt ethyl acetate & then seeding with xxlle of lactone acid (from I) into 2.13 g crude lactone acid mpt 165° and into 1.15 g gum (? malic acid) ∴ discard latter.

For analysis: the 2.13 g crude lactone acid was dissolved in 80 cc hot acetone & the filtrate concentrated to about 30 cc and then add acetic ether in small amt which deposited 0.35 g, crop I, tarry xxlle ∴ decant from these and then distill off a portion of the mixed solvent when got a separation of 1.37 g cp. lactone acid crop II in form of heavy prisms melting at 165°

0.1904 g dried in vacuo gave 0.2854 g CO_2 and 0.07978 H_2O

	Theory for $C_6H_8O_6$	Found
C	40.90	40.87
H	4.55	4.65

∴ pure lactone acid.

The filtrate from crop II gave 0.34 g more prac pure lactone acid.

Now took 1.87 g of cp. lactone acid & 1.2 g fused NaCl & 8 cc Essig. säure anhydrid & heated 9½ hrs (then distilled off on oil bath mixed acid) from 110°–120° and got (ether ext) 2.25 g gum containing xxlle (hot ether gave nothing more) On heating the 2.25 g extract on BWB in H_2O solution & finally evap on BWB in dest to small volume got a separation of 0.29 g cp. 2 oxy muconic lactone in yellowish plates m.p. 228–230° The aq. filtrate evap on BWB gave 1.45 g gum which again heated with 1.0 g fused NaCl & 5 cc H_2O acetic anhydride 8 hrs 100–120° gave 2.6 g gum + NaCl (90° 30 min) from which got by ether etc 0.15 g more xx $C_6H_4O_4$ there was probably still in there not formed by 2nd treatment with NaCl & Essig. anhydride ∴ yield of cp. body was 0.44 g from 1.87 g lactone acid.

Proof that body $C_6H_4O_4$ is identical with one obt from α galacto metasaccharinic acid (see No 55) is as follows. Took 0.299 g, crop I, & det rotation & heated it. and found α in 2 dc tube was ±0.0 absolutely. (a). 0.2823 g subst and 27.9872 g H_2O (∴ p = 1.0 ∠) 2-oxy muconic lactone took in cold (phenolphthalein) 0.2823 g – 2-oxy muconic lactone took in cold = 20.16 cc $\frac{n}{10}$ NaOH (theory for $C_6O_4H_3$—H = 20.16 cc $\frac{n}{10}$ NaOH)

(B) The H_2O solution of the 0.2823 g – 2-oxy muconic lactone took in cold 20.5 cc $\frac{n}{10}$ NaOH to get permanent pink coloration (theory for $C_6O_4H_3$—H = ...) & got as final result 20.5 cc $\frac{n}{10}$ NaOH to get permanent pink coloration; now add excess in all 43.02 cc $\frac{n}{10}$ NaOH & titrate back with $\frac{n}{10}$ HCl etc. (theory for $C_6O_4H_2$—H_2 = 40.32 cc). The aq. solution of a total of 39.12 cc $\frac{n}{10}$ NaOH used (theory for ...) ∴ had to add 1½ cc $\frac{n}{10}$ HCl to get rid of color & now the Na salt (theory 0.4074 g + 0.025 g NaCl) distilled off in vacuo got pink again ∴ 40.60 g H_2O ∴ p = about 1.0 & found α in 2 dc tube was dissolved yellowish gummy Na salt in H_2O so as to make ~~total wt = 40~~ & found α in 2 dc tube was absol ± 0.0. N_2O by to get back 2 oxy muconic lactone from aq. solution by adding 38.0 cc $\frac{n}{10}$ HCl etc & got back (40° vacuo) (ether ext) about 0.28 g yellowish (?) 2 keto hydromuconic gum (∴ can't get back 2-oxy muconic lactone): the yellow gum 0.28 g gave in H_2O solution with ph. hydrazine acetate a reddish semi solid oily ppt soluble in Na_2CO_3 & reprecipitated by dil acids ∴ may be the hydrazone of the 2 keto acid?

(55) Conversion of α galactometasaccharine into the α galacto metasaccharinic acid of Kiliani – det of its Space formula & conversion into 2 oxy muconic lactone June 4 09 Oct 13 09, May 15 + 14-10

Took 3.35 g cp. α galacto metasaccharin + 13.4 g HNO_3 (1.21) & heat 60° for 48 hrs & got 100° warm 3.6 g residue cont oxalic xxlle. This dissolved in 300 cc H_2O & add 1.0 g fused CaO & heat BWB 3 hrs gave 0.77 g wool $CaC_2O_4 \cdot H_2O$ & acid filtrate then digested with 0.2 g more CaO till faint alk. reaction & on standing over night aq. filt (vol 12) gave 2.4 g

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to 100cc)

plates +in conc aq. filtr (got

air dry xxlle of Ca salt, Ca $C_6H_8O_7$ 4H_2O in transparent

Buns [illegible] 4.5 g more same salt. The 2 crops Ca salts (2.85 g) treated with 1 L H_2O & 1.18 g oxalic 2H_2O

till partly dissolved Ca salt all converted into Ca C_2O_4 + got on dist off H_2O in vacuo, redissolving

in small amt H_2O + filtering etc + making aq. filtrate up to total weight 41.81 g + found α in

2 dc tube = +1°28. Now distill off H_2O again + got 1.72 g crude xx acid $C_6H_{10}O_7$ which on dissolving

in 5 cc H_2O + let stand gave large amt of transparent xx plates ∴ filter + conc aq. filtrate to small

crude acid mpt 150–153° (keep)

aq. filtr gave 0.4 g more

volume + got 0.9 g cp. acid in transp plates mpt dept 153° (Kiliani gives 146°) which

lost nothing in weight 18 hrs H_2SO_4 in vacuo; these gave $[\alpha]_D^{20} = +22°25$ (cf Kiliani).

i.e. 0.8828 g subst and 21.1852 g H_2O (∴ p =) d = 1.011 + found α in 2 dc tube = +1°,8.

Now take aq. solution + put in litmus + found could add 91.10 cc $\frac{n}{10}$ (0.999) NaOH when sol. became

faintly alkaline; the aq. sol. of $C_6H_8O_7Na_2$ salt (1.083 g theory) was distilled off vacuo + gummy

Na salt made up to total weight 27.1525 g (∴ p = 3.986) + found [α] in 2 dc tube = +1°54 ∴

$[\alpha]_D^{20} = +19°,11$. Now set free acid from Na salt + got back 0.5 g crude acid (Keep)

∴ Spacial formula of α galacto saccharin is COOH–C(OH)(H)–C(H)(OH)–C(OH)(H)–CH₂OH. Q E D

0.98 g Ca salts (dried vacuo)

Ca salt above gave on applying alcohol

The aq. filtrate from crop II which was probably a mixture of unchanged α galacto sacch aronic & α galacto saccharonic acids

which was probably a mixture of unchanged α galacto saccharin crude from various sources was heated

2nd Oxid expt. 6.7 g α galacto metasaccharin crude from various sources was heated with 1.0 1 L + got in taking 10 cc

40 hrs 40–45° with 26.8 g HNO_3 1.21 + then pour into H_2O + make up 1.0 1 L + got in taking 10 cc

141.6 cc $\frac{n}{10}$ NaOH needed ∴ treat rest of aq. sol with 5.3 g powd $CaCO_3$, 3 hrs Buns + got 2.48 g

CaC_2O_4 ½ & 5.3 g xx needles of α galacto saccharonic acid Ca $C_6H_8O_7$ 4H_2O (in 2 crops)

These with 2.1 g oxalic 2H_2O etc gave on extr 3 X with 600 cc ether only 1.0 g α galacto meta

saccharonic acid as transp glassy platten mpt 140–150°; the rest of the acid 2.0 g was

extracted as above by small amt H_2O etc + gums with 1.2 g powd NaCl + 8 cc acetic anhyd 10 hrs 100+110–120°

then distill off vacuo 90° 25 mm + take up in ether etc a total of 1.4 g gum + xxlle which

with cold ether gave 0.5 g xxlle which xx from H_2O gave 0.42 g cp. 2 oxy mucone lactone

in yellowish plates mpt 230°.

the 1.0 g crude acid (ether extract) gave 8 hrs 100–120° with 0.6 g powd NaCl & 4 cc Essig saure anhydrid

+ got distilling off 90° 25 mm + then extr with Ether etc 0.95 g crude gum + xxlle which treated with

H_2O on Buns + finally conc. in evap dish gave 0.2 g more cp. 2-oxy mucone lactone mpt 230° ∴ the

aq. filtrate gave 0.6 g gummy acid only (∴ have 2 reaction products always) the gum is easily

sol in cold H_2O & the xxlle are very difficultly soluble; thus the 0.62 g xxlle obtained from

all (3 g) α galacto meta saccharonic acid were xx from 12 cc hot water for analysis and got

very quickly while still hot a rapid separation of transparent very heavy yellowish tinted plates

mpt 228°–230° used for analysis & optical investigation). aq. filtr evap left 0.13 g more xxlle

found equally pure. Finally the combined gummy acid obtained from 3 g acid $C_6H_{10}O_7$ was

found to be 0.9 g + this heated again with 0.6 g NaCl & 3 cc acetic anhydride 8 hrs 100–120° etc

gave 90° 25 mm etc 1.61 g gum + NaCl, from which could get only 0.080 g more $C_6H_4O_4$ ∴ the gum

is an independent & main reaction product in all case when the meta saccharonic acids of the galactose as well as dextrose series when they are heated with NaCl + anhydride Q E D

II Brown salt after see Nov 10 – 09 not put in paper

0.1848 g $C_6H_4O_4$ dried H_2SO_4 in vacuo m.pt. 228°–230° $[\alpha]^{20}_D = \pm 0.0°$ gave
0.3484 g CO_2 and 0.0503 g H_2O

	Theory for $C_6H_4O_4$	Found
C	51.43	51.42
H	2.86	3.02

On mixing a small amt of this body with a corresp. amt. of $C_6H_4O_4$ obt from d dextro metasaccharin (see No 54, 0.29 g lot) found m.pt was 228°–230° ∴ bodies are identical.

(a) optical investigation: 0.2112 g substance and 20.8874 g H_2O (∴ p = 1.0+) and found α in 2 dc tube was ±0.0°. (b) titration; now titrate aq. sol. of 0.2112 g $C_6H_4O_4$ using phenolphthalein & found it took 15.5 cc n/10 NaOH in cold to get perm pink color theory 15.08 cc for $C_5H_3O_3$–COOH; now add in all 38.75 cc n/10 NaOH & heat & then titrate back with 9.78 cc n/10 HCl etc & got as final result 28.97 cc n/10 NaOH needed (theory 30.16 cc). Now distill off H_2O in vacuo & found got pink color ∴ had to add 1.5 cc more n/10 HCl ~~+ dry~~ got to get pink color to disappear then distilling off rest of H_2O & dissolving gummy yellowish Na salt in H_2O & making up to total weight 30.15 g found α in 2 dc tube to ±0.0° ∴ optically inactive $C_6H_2Na_2O_4$ salt Q.E.D.

Now set free acid by theory 27.5 cc n/10 HCl etc & got 0.2 g yellowish gum easily soluble in cold H_2O ∴ $C_6H_4O_4$ can not be recovered after conversion into di Na salt but got a yellowish gummy acid – ? 2 Keto hydromuconic acid – which in H_2O solution gave with pb. by means acetate an oily yellowish ppt., sol in soda, reppt by dil acetic acid – as was the case with a corresp. preparation of $C_6H_4O_4$ from d dextro metasaccharinic acid (see No 54)

(56) Conversion of β Galacto metasaccharin (Kiliani's Parasaccharin) into β Galacto metasaccharinic lactone acid & det of its Space formula. June 4 09 Jan 11–10

Took 3.15 g β Galacto metasaccharin gum (73.4 g HNO_3 (1.21) & heated at 60° for 48 hrs & got 95% 20 mm 3.3 g residue cont xx of oxalic (cf Ber 37, 3613 Kiliani): this dissolved in 500 cc H_2O & add 1 g Pbow CaO & then $BaSO_4$ gave 1.0 g mol. $CaC_2O_4 \cdot \frac{1}{2} H_2O$ & on heating filtrate with 0.15 g more CaO till perm. alkal sol + let filtrate stand got no xx of a Ca salt ∴ treat K_2C & evap when Ca salt finally came out as a gum (vol about 100 cc) when got very slowly a large (vol about 100 cc) ∴ redissolve by heat & let stand & scratch (vol about 100 cc) when got very slowly a large amount 1.67 g (air dry) of c xx heavy Ca salt $CaC_6H_8O_7 \cdot 5H_2O$ & on conc aq. filt. got 0.15 g more ∴ total 1.82 g: this with 0.71 g oxalic $2H_2O$ + 200 cc H_2O in $BaSO_4$ (in which Ca salt did not entirely dissolve) mpt 130°–153°, & dist off aq. filt. in vacuo gave 0.93 g crude xx lactone acid $C_6H_8O_6$ (theory 0.995 g): now took all of crude acid & titrate which gave $[\alpha]^{20}_D$ as –90° 45 found α in 2 dc tube = –7°327 (p = 4.006): now took all of crude acid & dissolve aq. solution (lactone): it took 53 cc n/10 NaOH in cold to get neutral (theory 54.3 cc) & on adding more alkali & warming solution got acid again & finally remained slightly ~~neutral~~ alkaline when theory (2 mols) NaOH = 108.6 cc n/10 NaOH had been added. The aq. sol dist off vacuo & take up Na_2 salt 1.292 g by theory in H_2O so as to make total weight = 32.3001 g (∴ p = 4.0) & found α in 2 dc tube = –1°414 ∴ $[\alpha]^{20}_D$ = –17°48.

Hence Space formula of β Galacto metasaccharinic acid is COOH–C(H)(OH)–C(H)(H)–C(H)(OH)–C(OH)(H)–CH₂OH Q.E.D.

Now add 110 cc n/10 HCl to Na_2 salt & distill off 50° 15 mm & take up in hot acetic ether & got back 0.98 g crude lactone acid of which 0.48 g were obtained pure mpt 159 to 160° from this solvent in conc & cooling (in H_2SO_4).

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~~and the less pure body~~ To get rid of a trace of NaCl in crude lactone, dissolved it in acetone, filter, distill off ether on adding sm. amt of ethyl acetate got 0.22 g more cp. lactone acid mpt 159–160° ∴ total amt. = 0.67 g pure body $C_6H_8O_6$ which now gave following constants: 0.6567 g substance and 15.7389 g H_2O (∴ p = 4.006) and found α in 1 dc tube = −3°97 ∴ $[\alpha]^{20}_D$ = −98°05

Now took aq. sol. of 0.6567 g substance, titrated in all 74.62 cc $\frac{n}{10}$ NaOH (= theory ∴ must have 0.8875 g $C_6H_8O_7Na$) & then distill off in vacuo & make up c H_2O to total weight 22.2447 g (∴ p =) & found α in 2 dc tube = −1°47 ∴ $[\alpha]^{20}_D$ = −18°23. Got back with 74.62 cc $\frac{n}{10}$ HCl etc. (acetone ex tr.) 0.6 g lactone acid which 3 cc essig. anhyd 100° 8 hrs gave 0.97 g acetyl derivative i.e. no $C_6H_4O_4$ is obtained unless NaCl is also present –

mpt 92° xx from ethyl acetate (Dec 30° 1908) $[\alpha]^{20}_D$ = +6°2 or +8°2

(57) Analysis of α dextro metasaccharin ; 0.2113 g substance gave 0.3420 g CO_2 and 0.1202 g H_2O

	Theory for $C_6H_{10}O_5$	Found
C	44.44	44.16
H	6.17	6.36

(58) The ~~conversion~~ of α galacto metasaccharin to β body by shifting of ∗ OH in α position Nov 15-09 cf Dec 6-09 (cf No 46 & 20). Jan 14-10 – Feb 7, 10

Took the 8.2 g cp. α galacto metasaccharine (Oct 2 & Nov 9 09) No 51 & heated in oil bath with inside temp ranging from 190°–197° & outside temp 192–200° for 7 hrs. Got a brown colored gum & small amt of H_2O noticed at top of d. f. ~~the dilug~~ dissolving gum in 5 cc absol. alcohol got 4.1 g α galact metasacch xx lle (well washed with cold alcohol) & then 0.25 g more. The alc. filtr. finally gave 3.55 g (100° 25 mm) gum which was acylated with 11 cc essig. s anhyd 100–110° 11 hrs & got 5.33 g gum of which 2.55 g tar (by diff) did not dissolve in ether & got from ether sol. acylated gums on 1x hydr with H_2O & 1x hydr with 5.0 g $Ba(OH)_2$ etc 1.95 g gum which xx from 4 cc absol. alc gave 0.63 g more α galacto metasaccharin & the 1.15 g gum obtained from alc. filtrate by 2.8 g Brucin etc gave 4.1 g xx salts which on xx from 100 cc 90% alc gave only 0.5 β galacto metasacch Brucin xx lle ∴ very incomplete transformation ∴ repeat at higher temperature –

Took 8.6 g xx lle mpt 140° & heated in solder bath outside temp 220° & inside temp ranging from 200°–210° for 9 hrs: small amt of H_2O appeared at top of d.f. & deep brown colored gum on acylation 100–110° 9 hrs with 28 cc anhydrid gave 13.9 g acylated gums of which 4.5 g tar remained insol. in hot ether. Got 9.75 g ether sol. acylated gums which hydr. 1x c H_2O & 1x 5.95 g with 10 g $Ba(OH)_2$ & 25 cc H_2O (8 hrs $BaCO_3$) gave 5.4 g gums; on diss. these in 10 cc absol. alcohol got 1.67 g xx α galacto metasaccharin & then on dist off on dissolving in small amt glalcohol got 0.38 g more of similar xx lle (∴ 2.05 g total), alc. filtr now gave back 3.3 g gum which with 8.0 g Brucin etc gave 12.3 g salts & these xx from 50 cc alcohol 98% gave rapidly 5.02 g β galacto metasaccharin c Brucin xx lle in delicate needles; Kristen mpt 130–136 – The alc filtr gave no more xx lle ∴ set free gum by 5 g $Ba(OH)_2$ & got 3.95 g Brucin & 1.9 g gum which converted by Strychnine into salts gave no xx lle ∴ set free gum & acylate 7 hrs 100° with 6 cc anhydrid & got 2.68 g acylated gum s-ar and found this left 0.53 g insol tar on digestion with ether – The hydr. of ether sol acylated gums 1x c H_2O & 1x with 5 g $Ba(OH)_2$

($p = 3.84$)

gave back 1.2 g gum whose $[\alpha]_D^{20} = -14°4$ only, ∴ another body present besides the α + β metasaccharinis whose $[\alpha]_D^{20}$ must be either slightly − or +.

The 1.2 g gum dissolved in alcohol ... and gave 0.2 g α galactometasacch. xxlle & the rest of gum left in alc filtr 0.95 g (act. det.) gave with 2.3 g Brucine etc 3.2 g salts which xx from 6 cc alcohol gave 0.83 g more β Galactometasacch. Brucine xxlle m.pt. decpt 120°–137°.
Needle filtr was now lost by an accident ∴ unknown body (about 0.6 g) probably, cont CH=CH ... could not be further studied.

Proof that β galactometasaccharin was formed; took the 2 crops of crude Brucine salt 5.02 g and 0.83 g ∴ 5.85 g and got by xx from 2 cc H_2O + 35 cc absol. alcohol 4.09 g desti xxlle m.pt. decpt 130–137° & $[\alpha]_D^{20} = -26°2$ i.e. 1.018 g subst and 24.445 g H_2O (∴ $p = 4.0$) and found α in 1 dc tube = $-1°06$. (alc. filtr discarded cont 1.65 g salts) (it gave 0 by xx from ½ cc H_2O & 10 cc alc)

The 4.09 g β salt gave with 2.0 g $Ba(OH)_2$ etc 2.58 g Brucine and 1.16 g gum (alc extr) which could not be got solid ∴ digest it $BaCO_3$ with excess Strychnine 8½ hrs $BaCO_3$ & found 1.88 g dissolved then got 3.75 g gummy (50° 25 mm) salt which xx from 1 cc H_2O & 8.5 cc alcohol gave 1.63 g crop I and 0.46 g crop II ap. β Galactometasaccharinic Strychnine in flat needles m.pt. decpt 120°–130°.
Crop I gave $[\alpha]_D^{20} = -23°43$ i.e. 0.9903 g subst and 23.6986 g H_2O ∴ $p = 4.013$ & found α in 2 dc tube = $-1°9$ [cf. No]; the 2nd crop 0.46 g β salt was obt by digesting alc filtr crop I again for 9 hrs $BaCO_3$ with excess Strychnine etc. (& then alc filtr from crop II salt was discarded).
Now take the combined crops I & II of β Strychnine salt & got by 1.0 g $Ba(OH)_2$ etc 1.24 g Strychnine & 0.68 g (alc extr) β gum which gave $[\alpha]_D^{20}$ ($p = 3.995$) = $-46°9$ i.e. found α in 2 dc tube = $-3°77$. Now distill off H_2O & got back 0.62 g gum & this gave with 0.7 cc ph. hydrazine & 0.7 cc alcohol within 1½ hrs a mass of xx hydrazide; after standing at. 24 hrs add ethyl acetate till all powdered & got 0.51 g yellowish β galactosaccharinic ph. hydrazid m.pt 85–90° (analysed for C, H, & N by Upson). This gave $[\alpha]_D^{20} = -2°23$ i.e. 0.5017 g subst and 12.0702 g H_2O ∴ p = 3.99 & found α in 1 dc tube = $-0°09$. The hydrazid decomposes in all cases rapidly on standing [cf No 59] Q.E.D. identity with β Galactometasaccharin from d. galactose & 33% NaOH.

(59) Galactose + 33% NaOH final, continued from No 51. Jan 14–10 Feb 7–10 and May 19–10 (Dec 18–09)

On boiling the 2.7 g gum ($[\alpha]_D^{20} = +4°07$) due to presence of dextrose in d. galactose with 6.5 g Brucine got 9.6 g salts which xx from 15 cc alcohol got solid with xxlle crop I m.pt 100–135° = 2.82 g probably a mixture of α + β galactometasacch salts.
to prove this took the 2.82 g crop & got $Ba(OH)_2$ etc 0.73 g gum (alc) with $[\alpha]_D^{20} = +2°72$ ∴ this can't be said a mixture but body was probably β Isosaccharin. Now got back gum 90° in vacuo & extr with acetic ether & got 0.52 g gum $[\alpha]_D^{20} = +3°95$ which with 1.2 g Brucine etc gave 0.33 g crop I salt m.pt 140°–150° = porous salt (discard) N.B. the β Isosaccharin should give a porous salt like l. erythro & gum & m.pt should be over 180° but too small an amount present to isolate it as a pure product. The alc filtrate from crop I salt gave back with $Ba(OH)_2$ etc 4.02 g Brucine + a gum which extr R.T. 2x with 1 L ether gave 1.45 g gum $[\alpha]_D^{20} = +7°79$ ($p = 4.0$) and on extr

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residue still further with ethyl acetate got $\underset{Thus}{0.37}$ g more gum ($\therefore$ discard found $\pm$ $p = 4.0°$),

The 1.4 g gum $[\alpha]^{20}_D = +7.79$ boiled R.F. H_2O with 2.8 g Cl Quin alc gave 4.4 g gummy salts which dissolved easily in 10 cc absol alc & gave nothing on cooling $\therefore$ α Isosaccharin can't be present i.e. has been entirely removed in previous operations. Got back $Ba(OH)_2$ etc 0.87 g gum (see le ether extr) titrated with 2.0 g Brucin & xx salt obtained & got 0.37 g previous salt crop I m.pt 190°–195 " " which must have been the β Isosaccharin discard material at this point

Brucin (see p 80).

The 4.85 g ± gum (bottom p 69) heated R.F. with 30 cc ethyl acetate shake & cool gave 2.37 g soluble gum $[\alpha]^{20}_D = +2°.47$ $p = 4.0$ titrated for C6 lactone (discarded).
and 2.80 g insol gum $[\alpha]^{20}_D = -1°.73 \rightarrow$ 0.87 g acc. det
An extr the 2.37 g lot R.F. 2x with 200 cc ether found all but ~~1.0 g (by diff)~~ dissolved & found in ether solution 1.5 g gum with $[\alpha]^{20}_D = +5°.52$; the 0.87 g lot gave $[\alpha]^{20}_D = -2°.72$ $[\alpha]^{20}_D$.
& this digested with 3.6 g Brucin gave 5.1 g salts from which got on xx from 6 cc absol. alcohol 0.7 g xx needles m.pt 188°–205° [? β Isosaccharinic Brucin] probably: got crop II 0.82 g m.pt 155°–165°. discarded all material at this point – but observations clearly show presence of β Isosaccharin ~~an~~ a + rot. saccharin with high melting Brucin salt (as this body is α oxymethyl l. erythro C5 gum) besides α & β Galactometasaccharin.

β Galactometasaccharinic Brucin: had a total of 51.89 g crude β Brucin salts as follows (see No 51)
18.28 g + 7.24 g + 11.75 g + 4.35 g + 10.27. On xx this from 17 cc H_2O & 250 cc alcohol got 27.16 g crop I β Galactometasacch Brucin m.pt decpt 130–140° $[\alpha]^{20}_D = -25°6$ ($p = 4.015$): this gave with 12 g $Ba(OH)_2$ etc 17.77 g Brucin & 7.47 g crude β galactometasaccharin gum (alc extr), : it was now digested R.F. 14½ hrs (in 2 operations powdering 2nd time) with an excess Strychnine & found 13.16 g Strychnine had dissolved & got 26.25 g xx salts which dissolved in 5 cc H_2O & 40 cc alc gave 11.42 g cp. β Galactometasacch. Strychnine xx lle m.pt decpt 125–130° $[\alpha]^{20}_D =$
$-23°.48$ 0.9136 g salt and 21.9049 g H_2O ($\therefore p = 4.003$) gave α in 2 dc tube $= -1°.90$.
got 3.09 g crop II m.pt 115°–125° & alc filtrate boiled again with Strychnine took up 1.27 g and then gave 3.64 g more crop III β Strychnine salt m.pt decpt 120–130°: (alc filtrate now discarded),
Got by uniting crops I II & III β Strychnine salts = 17.15 g with 9.0 g $Ba(OH)_2$ etc 11.0 g Strychnine and 5.46 g (alc extr) β Galactometasaccharin gum which did not get solid on seeding with (β xx obtained Nov 25 08) but gave $[\alpha]^{20}_D = -49.7°$ $p = 4.0$ (found α in 2 dc tube $= -4°.02$.),
$\therefore$ gum is a mixture of lactone & acid? free acid or other anhydrides.]. Now make up with H_2O to 500 cc & took 100 cc for ph. hydr. expt and ~~1~~60 cc for rotation of Na salt.
Rotation Na salt: 60 cc $\therefore$ 0.6553 g lactone should give 0.8170 g $C_6H_{11}O_6Na$ $\therefore$ treated with 40.45 cc $\frac{n}{10}$ NaOH & heat on Bu_2O. then distill H_2O from just neutral (to litmus) solution at reduced pressure & dissolve in H_2O

to total weight 20.425 g and found (∴ p = 4.0) α in 2 dc tube = −0°.31 hence $[\alpha]_D^{20}$ = −3°.833.

Phenylhydrazide 100 cc of solution ∴ 10 g distilled off 100° 20 mm & heat gum in cold with ice ph. hyd
+1 cc alcohol soon got entirely solid (within 3 hrs) with snow white nodules (without scratching). after 20 hrs standing of.
add ethyl ethyl acetate break up lumps & got 1.61 g almost white ph. hydrazide m.pt 85–90°
(analyzed for C H & N by Upson) — which is a very unstable hydrazide & can't be got without much loss
be xx from (ale or (small amount) from mixture of) alcohol & ale ether. ∴ det $[\alpha]_D^{20}$ of crude product directly after drying
H_2SO_4 in vacuo as −1°.92 i.e. 0.5898 g subst and 14.190 g H_2O ∴ p = 3.99 & found
α in 2 dc. tube = −0.155.   Rest of β Galacto meta sacch. gum 3.76 g was used up in
a 2nd oxid to β galacto metasaccharinic acid May 19–10 McLeod book II but not worked up
or described in these sheets.   β Galacto metasacch Brucin (p 81) still contained 24.73
The alc. filtrate from the 27.16 g crop I β Galacto metasacch ... salts m.pt 110–140° ∴ a mixture of
g Brucin salts syrup on xx from 4 cc H_2O + 50 cc alcohol 9.85 g crop II ... $Ba(OH)_2$ & got 16.11 g Brucin & 6.55 g gum (alc ext)
α & β Galactometasacch. Brucin ∴ treat all with 10 g ... α Galacto metasaccharin xx lle
which dissolved in 7 cc alc & add then 6 cc ethyl acetate gave 0.87 g $[\alpha]_D^{20}$ = −11°.88 (p = 4.0) which with 13.1 g
m.pt 135°–140°. alc. filtrate gave back 5.4 g gum ... crop I of a porous Brucin salt m.pt
Brucin alc gave 20.1 g gummy salts from which got 7.83 g ... only 3.86 g β Galacto metasacch. Brucin
135°–150° ... from 2 cc H_2O + 35 cc alcohol got ... salts which xx from 15 cc absol. alcohol gave
m.p. & cpt 135°–140° (keep); the alc. filtrate gave 3.8 g xx salts which melted from 150–153°
1.78 g of a Brucin salt (with soft feel) cont xx H_2O & after drying H_2SO_4 in vacuo (wt 1.78 g) & titration of the gum
and had $[\alpha]_D^{20}$ = −21°.72; this gave $Ba(OH)_2$ alc 0.46 g gum $[\alpha]_D^{20}$ = −5°.69 (p = 4.0) 3.076 cc $\frac{n}{10}$ NaOH (theory for C₆ lact = 28.4 cc)
The orig. alc. filtrate from crop I 7.83 g 0.46 g took in all ... salt should contain about 11.5 g salts ... xx from 30 cc alcohol
gave 3.57 g crop II salts m.pt 110–120° $[\alpha]_D^{20}$ = −19°.75 ∴ mixture of α & β meta sacch Brucin
now discard all material as could go no further.
It is obvious that above was a mixture of (α?) β Isosaccharin & of α & β Metasaccharins

(60) On the conversion of α dextrometasaccharin to β by shifting {May 25-09 / Feb 3-10 / April 10-10}

heated d.f. in a solder bath outside temp
Took 6.18 g xx α lactone from 8.0 g (9.18 g) of Ca salt (No 52) ... Now acylate with 20 cc anhydride for 9 hrs
215° ... 200–210° for 9 hrs: a little H_2O ... in d.f. ... mol. in hot ether. got 7.07 g etherol acetylate
100° & got 9.73 g acylated gum of which 3.0 g ... (by diff) ... 3.9 g (alc extr) gum S, which
gum which hydr. 1 x C H_2O → 4.72 g & then with 10 g $Ba(OH)_2$ + 35 cc H_2O gave 11.25 g Strychnine salts which xx from 3 cc H_2O
digested 9½ hrs with excess Strychnine took up 6.48 g & gave ... Strychnine m.p. & cpt 180°–190°; alc filtr
+ 30 cc alc. alcohol gave 2.67 g crude α dextrometasacch. Strychnine for 5½ hrs ... took up 0.61 g alkaloid & then
distilled off & heated again with excess Strychnine ... 1.35 g crop II crude α dextrometasacch
gave 9.15 g salts which (warmed with) xx from 1 cc H_2O + 20 cc alcohol ... 2.0 g $Ba(OH)_2$ 1.28 g
Strychnine crop II m.p. & cpt 170°–180°. Crops I + II = 4.02 g, gave with ... $Ca(OH)_2$ alc ... a total of
crude α dextrometasacch. (not entirely) xxc gum (alc ext) from which got by
1.05 g cp. anhydrous xx Ca salt → Q.E.D.
The alc filtrate from crop II Strychnine salt gave with $Ba(OH)_2$ alc 3.97 g Strychnine and
2.43 g crude β dextrometasacch. gum which on seeding got a fair crop of xx lle but another subst besides α is present as shown by what follows:

(83)

Treated gum with 5.91 g Brucin & got 9.1 g xx salts which xx from 20cc alcohol soon got solid with xx lle on seeding with β dextro Brucin xx lle: got 4.4 g wt. decpt 120°–150° after drying in vacuo with $[\alpha]^{20}_{D} = -22.03$ 1.2. 0.8608 g salt + 20.6842 g H_2O ($p = 3.995$) and found α in 2dc tube = −1°78. the settling free gum from this by 20 g $Ba(OH)_2$ etc got 2.74 g Brucin and 1.32 g gum (alc extr) which would not get entirely solid even on seeding with β dextrometasacch xx lle ∴ converted it into Strychnine salt B.W.B. 8 hrs took up 2.2 gms Strychnine & gave 3.63 g gummy salts from which by dissolving in 1cc H_2O + 20cc alcohol seeding with β salt could get no separation of xx salt ∴ set free gum by $Ba(OH)_2$ & got back 1.15 g gum whose $[\alpha]^{20}_{D}$ was −2°97 ($p = 4.0$) α found in 1dc tube = −0.12° ∴ another substance which must be strongly laevo, probably. $COOH\,CH{=}CH\,\overset{OH}{\underset{H}{C}}\,\overset{OH}{\underset{H}{C}}\,CH_2OH$, must be present. Now distill off H_2O in vacuo & treat gum with 1cc alc & 1cc ph. hydrazine & got 3 days O.T. seeding with β ph. hydr., and ~~a total~~ rubbing with 2cc alc + 2cc acetic ether only 0.090 g xx mpt 100°–105° which were obviously identical with β dextrometasaccharinic phenylhydrazide [see No], for it xx from alcohol in transparent plates.

The alc. filtrate from crop I Brucin salt gave 3.85 g salts from which by xx from 10cc alcohol got on long standing 1.83 g new Brucin salt $[\alpha]^{20}_{D} = -23.3$ mpt 130°–140° this by $Ba(OH)_2$ etc gave 0.47 g gum (alc extr) from which by 0.5cc ph. hydr. & 0.5cc alc got only 0.01 g ph. hydrazid mpt 100°–105° as above [∴ write & keep].

It is obvious from all this that best way to prove α & β Dextrometasaccharins are space isomers differing only in position of OH group on α carbon alone is to convert the β body by heat 200–210 into the α as it can be isolated pure as shown above.

(61) Oxid. of d threo C_5 gum to d. 1,3 dioxy glutaric acid Nov 22, Dec 16 09 Jan 12–10

Took the ~~5.8 g~~ 5.75 g cp. laevo gum (April 14–09)(No. 34 p 46 top) (Oct 2–09 No 50 p. 66 bottom) $[\alpha]^{20}_{D} = -40.37$ & dissolved it in 23.2 g HNO_3 sp.gr. 1.21. & heated 48 hrs in bath kept between 60–64° & then distill off in vacuo finally at 90°–95° at 25 mm & got 4.1 g residue cont. oxalic acid xx lle. Dissolved this in H_2O & treated B.W.B. with 1.0 g powd CaO & got 1.6 g $CaC_2O_4\,\frac{1}{2}H_2O$ and some $Ca(OH)_2$. The filtrate heated with 0.1 g more CaO powd & finally the faintly alk. solution was conc. to see if can get a xx Ca salt n.g. ∴ had to ppt Ca salts from conc aq. sol by alcohol and 4.7 g ppted Ca salts (a in portion) washed with alc & ether air dry which lost 0.45 g in weight over H_2SO_4 in vacuo 2 days & then gave 21.36% CaO on ignition (i.e. 0.2327 g gave 0.0497 g CaO 2x ignition) ∴ treated rest of salts 4.038 g with H_2O to total weight 100.95 g (∴ $p = 4.0$) & found α in 1dc tube = +0.28° ∴ $[\alpha]^{20}_{D} = +6.925$; now ppted Ca by 1.941 g oxalic $2H_2O$ & got (alc extr) after distilling off H_2O at 25 mm & 30° 2.8 g gum which was now digested B.W.B. 5 hrs with 12.4 g Chinin (leaving 2.28 g unsol Chinin). The Chinin salts mpt 160–5° diff sol. in H_2O (easily soluble on conc to small volume) were poured by alk. solution on conc gave in 3 crops a total of 6.37 g (5.3 g + 0.82 + 0.25 g). The xx salts left in H_2O ~~to~~ leave some unchanged d. threo C_5 chinin salt, after distilling off H_2O in vacuo 95° xx from alcohol (30cc), as got 0.75 g salt mpt 171–2° 0.025 g crop II mpt 174°) & got from rest by $Ba(OH)_2$ etc 1.05 g gum containing xx lle ~~acid~~? of malonic acid?

(see next page)

The 6,37 g diff sol in H_2O Chinin salts gave with 5.0 g $Ba(OH)_2$ etc 5.2 g Chinin and
1,15 g gum containing xxlle. This was extracted R.T. 2 x with 400 cc Ether when all except
0,15 g by diff had dissolved + on conc. the ether solution on WB to a small volume got a separation
of 0,38 g cp. 1,3 Dioxy glutaric acid in snow white heavy xxlle melting sharply at 135° to
a liquid and giving off water vapor (after washing with cold ether). The ether filtrate gave back 0,6 g gum which was probably
a mixture of d. malic and 1,3 Dioxy glutaric acids — but these could not be separated :: discarded.
The 1,05 g gum obtained from easily sol. Chinin salts dissolved easily except 0.11 g tar in hot Ether
(3 x 100 cc) & gave 0,45 g gum containing a xx subst subliming in xx at sides of d.f. which were probably
malonic acid — for on digest. gum BWB with 0,5 g pure cad & conc aq. filtr (Vol 300 cc) to a smaller volume
got a rapid separation of 0,4 g diff. sol. Ca salt lost material on treating it with 0.28 g oxalic acid
(?) + ~~look up~~ o.K. —
but xx of malonic at this point.
The 0,38 g cp. 1,3 Dioxy glutaric gave $[\alpha]^{20}_D = -2{,}614$ i.e. 0.3782 g and 9.1404 g H_2O (:: p = 3.974)
and found $[\alpha]$ in 1 dc tube $= -0{,}105$. Titration like a free dibasic acid: it took up at once in cold
45 cc $\frac{n}{10}$ NaOH solution ... acid (litmus): now ran in a total of 49,3 cc $\frac{n}{10}$ NaOH solution
... on long boiling on W.B. Theory for $C_5H_8O_6$ 0,3782 g = 46,12 cc (and for ... the xx ...
$C_5H_6O_5$ would be 51,81 cc). The alkaline solution was now distilled off in vacuo and the ... weight 11,990 g and found α in 1 dc tube
$C_5H_6O_6Na_2$) with H_2O to total weight 11,990 g and found α in 1 dc tube
left (theory = 0.4798
was +0,9 :: $[\alpha]^{20}_D = +22{,}25$. To get back free 1,3 Dioxy glutaric acid again the Na salt was
now treated in aq. sol. with 50,3 cc $\frac{n}{10}$ ~~NaOH~~ HCl (:: 1 cc $\frac{n}{10}$ HCl in excess) then distilling off H_2O /
in vacuo finally heating to 95° at 25 mm etc got back by Ether R.T. etc 0,38 g gum my acid only /
:: a change took place probably due to presence of excess HCl at 100° [cf. galacto & ... to
metasaccharinic acids towards lactol & ... anhydrid at 100°]. This gum treated with Chinin
took up 1,4 g alkaloid on conc. aq. filtr, & got a separation in all of 1,53 g xx ... sol in
H_2O salts (and last aq. filtr cont pract nothing) :: the gum was now set free from these
salts by 1,0 g $Ba(OH)_2$ & got back 3 x 100 cc hot Ether ... ether. sol. to small volume
only 0,060 g 1,3 Dioxy glutaric xxlle & besides 0,25 g gum which was probably a mixture
of 1,3 Dioxy glutaric and of d. 1-oxy glutaconic acid. The gum gave finally with 1,35 g
(Keep) 0,73 g of a Brucin salt, cont xx H_2O, swelling
Brucin etc on xx salts obtained from 5 cc alcohol N.B. The Brucin salt of d. 1,3 Dioxy glutaric
after drying H_2SO_4 in vacuo between 120 – 125° — whereas the of Kiliani props of l. 1,3 Dioxy glutaric
melts at 242° is very diff sol. in abs alcohol —
acid — Ber 40 1238 — :: Took 4,851 g lactone $[\alpha]^{20}_D = -36°5$
2nd oxidation was now necessary to get d. 1,3 Dioxy glutaric acid for analysis (cf Feb. 25 - 1910) then made up c H_2O to a ... & took
[June 22, 10 of No 68] + 19,4 g HNO_3 1.21 & heated 45 - 50° for 48 hrs; BWB with ~~H_2O~~ 3,5 g (theory 3,34 g)
20 cc & poured 18,43 cc $\frac{n}{10}$ NaOH needed :: treated rest of aq. filtrate with $CaCO_3$ + H_2O and ... and $Ca(OH)_2$ &
pour) $Ca(OH)_2$ till alkaline solution (goes quickly) & got 1,73 g ... 3,75 g air dry w
alk. filtrate was then conc to small volume on WB, & ppted by alc etc gave 0.047 g CaO).
3,32 g vacuo dried Ca salts latter containing 22,91 % CaO (0.2051 g salt gave ... equal ...
:: treat rest of salts 3,1625 g with 1,630 g oxal ac 2 H_2O & got on treating aq. filtrate with
(after determining $[\alpha]^{20}_D$ of a portion of Ca salt (p = 4.0) to be + 9°92)

(85)

8.4 g Chinine etc a total of 5.38 g diff sol in H_2O Chinin salts m.p. 165-7° (apparently air dry)
these gave with 3.0 g $BaCl_2$ etc 4.17 g Chinin + 3 x 500 Ether R.F. or conc a total of previously treated well with cold ether
0.25 g d. 1,3 Dioxy glutaric acid m.p. 135° (Ether H_2SO_4 in vacuo)
0.2105 g substance gave 0.2830 g CO_2 and 0.0950 g H_2O

	Theory for $C_5H_8O_6$	Found
C	36.59	36.65
H	4.88	5.01

Got 0.55 g gum from ether filtrate which with 3.25 g Brucine etc gave 4.65 g xx salts which
xx from 12 cc abs. alcohol gave 2.09 g crop I salts m.p. 130-160° opaque nodules, which
on digesting with 20 cc abs. alcohol left 0.63 g mostly II d. 1,3 Dioxy glutaric Brucin (?)
m.p. 235-238° [Keep] - discard rest of salts ? since II Brucin d. 1-oxy glutaconic
present but no indication of d. Malic acid. Dec 16 - 09

(62) Properties of l. Malic acid, free acid, Na_2 salt, Brucin & Chinin salts.

Solubility, l. Malic acid, 2 g, CaZK's dissolved easily R.T. in 5 cc ethyl acetate & on cooling came out again in part in
xxlle; 2 g. l. Malic acid dissolved easily R.T. in 100 cc Ether & on dist off of solvent on WB to a small
volume got a separation of 0.84 g heavy xxlle m.p. 100° (in vacuo drier) with $[\alpha]^{20}_D = -2°.16$ i.e.
took 0.822 g and 19.7058 g H_2O (∴ p = 4.004) & found α in 2 dc tube = -0.175.
Titration: on adding 122.77 cc $\frac{N}{10}$ NaOH solution became very slightly alkaline (theory = 122.7 cc) & on
distilling off H_2O in vacuo & taking up Na_2 salt. theory = 1.092 g to total weight 27.30 g with H_2O
∴ p = 4.0 found α in 2 dc tube was -0.675 ∴ $[\alpha]^{20}_D$ of $C_4H_4O_5Na_2$ is -8°.35.
Chinin salt, 1 g l. Malic + 5 g Chinin BaB gave on letting hot solution (Vol 200 cc) stand
a separation of 4.50 g, crop I, l. Malic Chinin in transparent xx needles m.p. 182 (Keep)
∴ 67% comes out + salt is fine for detecting traces of d & l Malic (see No 63),
the salt also xx well 1.61 g from a hot sol. of 1 cc H_2O & 10 cc alcohol coming out in transp
needles in very large amounts.
II Brucin salt, 1 g l. Malic & 5.88 g Brucin on BaB with H_2O quickly gave a clear solution
& on dist off H_2O in vacuo freed the 10 g salt dissolved in 10 cc Hot H_2O & on cooling got a separation
of 1.67 g xxlle in transp. needles m.p. 220° (Keep) ∴ only small amt. comes out from H_2O -
the salt however is very very diff sol. in boiling alcohol R.T. & on cooling got a separation of
heavy transparent needles -
II Ca salt. took 1 g l. Malic acid & 0.5 g pure CaO in BaB & got rapidly a (clear sol ~~ation~~ practically Vol 175 cc
& on ~~filtration~~ cooling ~~some~~: got no sep. of xxlle; but ~~none in watch~~ none on BaB in open dish the anhydrous II Ca salt
separates out rapidly in form of heavy xx granules: got (in 3 crops) a total of 1.17 g (theory
1.28 g) but must first evap. to dryness & then take up in cold water to get all of Ca salt
out as it stays in eq. solution to large ex tent otherwise.

(63) (86) April 18-10

The absolute space formula of d. 1,3 dioxy butyric acid is $COOH \cdot C(OH)(H) \cdot C(H)(H) \cdot CH_2OH$.

Formose (30 20) Formose $CaCl_2$

March 1, April 1, 10 d

Took 50 g xx 1,3 Dioxybutyric phenylhyd mpt 128°-132° from various sources also from previous l. arabinose + l. xylose expts + treated with 200 cc H_2O + 80 g $Ba(OH)_2$ 7 hrs B.W.B. + got dioxybutyric ... 22.4 g gum (cold ether extr). This boiled with H_2O + 80 g Brucine (theory 86.5 g) gave an acid solution + then distilled off so as to leave 100 cc H_2O + 102 g salts + got 34.34 g crop I xx plate of d. dioxybutyric Brucine (dried H_2SO_4 in vacuo: not all xx H_2O off). On xx this from 44 cc H_2O got 26.48 g xx plates averaging which lost 3.23 g H_2O on drying H_2SO_4 in vacuo to constant weight ∴ 12.20 % (theory for $4H_2O$ = 12.30 %)

The anhydr. salt gave $[\alpha]_D^{20} = -20{,}58$ i.e. 1.1720 g substance + 28.2293 g H_2O ∴ p = 3.987 gave α in 2 dc tube = -1,66.

The anhydr. salt with 10 g $Ba(OH)_2$ got 19.2 g Brucin + 4.17 g gum.

Now took 23.25 g of the anhydr. salt with 10 g $Ba(OH)_2$ ... then pour into H_2O + make up to 1 L + titrate oxidized with 16.8 g HNO_3 1.21 for 45 hrs at 45°-50° ... for 20 cc of sol required 26.8 cc $\frac{n}{10}$ NaOH + on testing ... found much free HNO_3 present ... (5 hrs B.W.B.) got no ppt ... calcium ... on conc. aq. filtr. got no ppt of Ca salts ∴ ppted Ca'' by aq. sol with 5.0 g powd $Ca(OH)_2$ ... got no ppt of Ca salts ∴ ... xx of Ca oxalate + on adding alcohol to conc. aq. sol. got no ppt of Ca salts ∴ ppted ... much HNO_3 8.2 g oxalic $2H_2O$ + on distilling off in vacuo finally in a small d. f. released ... on dissolving in H_2O went off (bath 70° 75° ...) - got 5.5 g residue cont. xx the oxalic + on dissolving in H_2O to 500 cc + take 10 cc found 9.86 cc $\frac{n}{10}$ NaOH needed ∴ treat rest of aq. sol. with 1.8 g powd $Ca(OH)_2$ on boiling W.B. + conc. aq. filtr to small volume + ppte Ca salts by alcohol etc ; got 5.14 g vacuo dried salts (cont. 21.72 % CaO by analysis) ∴ treat rest 4.9535 g with 2.4 g oxalic $2H_2O$ + then treat aq. filtr with 12.3 g Chinin + got (xx from H_2O) 4.74 g Chinine d. malate mpt 165°-170° in 2 crops probably containing some other salt, which with 3.0 g $Ba(OH)_2$ etc gave 3.9 g Chinin and 0.65 g xxlle (ether Extr R.7.). From this got on powdering + washing on ... with dry. and dry ether 0.38 g d. Malic acid mpt 98°-100° with $[\alpha]_D^{20} = +3{,}07$ i.e. 0.3743 g subst and 8.9213 g H_2O (∴ p = 4.027) gave [α] in 1 dc tube = + 0,125.

Titration: the H_2O solution of the 0.3743 g acid (...) took up in cold alone 55.9 cc $\frac{n}{10}$ NaOH (= theory) $C_4H_4O_5Na_2$ should now be present. Distill off H_2O in vacuo + make up c. H_2O to total weight 13.7576 g (∴ p = 3.613) and found α in 1 dc tube + 0,30 whence $[\alpha]_D^{20} = +8{,}29$ (cf. l. ... No 62 - 8,35). Now add 53.9 cc $\frac{n}{10}$ HCl to $C_4H_4O_5Na_2$ salt + got back ... distill off H_2O in vacuo + ext to R.7. with ether 0.32 g d. Malic acid. Took 0.1 g of this and mixed with 0.1 g l. Malic (No 62) + dissolved in H_2O and got distilling off H_2O etc 0.2 g dl Malic xxlle mpt 115-125° - or (after washing + warming powd xxlle) got 0.1 g dl Malic acid mpt ~~128~~-130° (Keep) Q.E.D.

of Kiliani (Ber 18 2514, 38 2672, 3624, 40 1238)

(64) Oxidation of α Isosaccharin by HNO_3 etc

Dec 1-09 ; Jan 17-10

Tried to get meso + l. 1,3 Dioxy glutaric acids from α Isosaccharin + HNO_3 directly.

Expt I 10 g α Isosaccharin mpt 94° + 40 g HNO_3 1.21 heated in d.f. 48 hrs at 60°-65° + then distilled off H_2O + HNO_3 temp never over 50° at 25 mm + got 10.3 g gummy residue which boiled at 130° for 10 hrs with 50 cc H_2O gave much CO_2 + got back 100° vacuo 7.45 g gum cont xx oxalic. Boil this gum with H_2O + 2.5 g powd $CaCO_3$ and got 1.57 g insol $CaC_2O_4 \frac{1}{2}H_2O$ ∴ conc aq. filtr to 150 cc but got no xxlle ∴ add 0.2 g powd. CaO heat B.W.B 2 hrs when nearly all CaO (and dissolved) + conc to 50 cc could get no xxlle of meso dioxyglutarate of Ca ∴ ppte Ca by 4.5 g oxalic + got back 6.55 gum

The University of Chicago

The 6.55 g gum was resolved by thorough digestion with much ethylacetate into 3.9 g soluble and into 2.2 g insol tarry gum & the latter digested BaCO3 with 9.0 g chinin this gave 2.7 g insol

Chinin & got from aq. filtrates on conc etc a total of 5.28 g 1.0 g I; 2.61 g II ppt 160–50°; 1.17 g III & 0.45 g IV in 4 crops. The aq. filtr conc the easily sol in H2O chinin salts gave with 5.0 g $Ba(OH)_2$ etc 1.9 g chinin & 0.9 g gum of which 0.55 g dissolved in hot acetic ether & 0.35 g tar (discard) remained insoluble –

Treatment of the 3.9 g gum in a similar way took up 13.36 g chinin & got a total of 7.11 g [1.08 g I; 3.55 g II; 1.98 g III & 0.5 g IV] (diff soln H2O) chinin salts. The easily sol in H2O chinin salts left in H2O solution gave with 10 g $Ba(OH)_2$ etc 7.28 g chinin & 2.3 g gum of which 2.05 g easily dissolved in hot acetic ether & 0.25 g tar (discard) remained undissolved. Unite the 2.05 g with the 0.55 g gum ∴ 2.7 g gum containing a xx lle substance & found on digestion with ether R.T. 2X 200 cc all but 0.45 g insol. yellow gum dissolved

Unite this with the gums obt from diff sol in H2O chinin salts. Total chinin salts diff sol in H2O obtained were 5.28 g + 7.11 g; These treated with 10 g $Ba(OH)_2$ etc gave 7.28 g chinin + 2.85 g gum of which 1.85 g easily dissolved in hot acetic ether & 0.20 g tar (discard) remained insoluble. The 1.85 g gum and 0.45 g gum above was digested BaCO3 with 1.0 g pure CaO (4 hrs) & filtered from 0.75 g CaO and ? meso Ca salt & on conc aq. filtrate got a total of 1.1 g xx Ca salt (diff sol in H2O) in plates; this however when boiled BaCO3 with 0.63 g oxalic 2H2O etc gave only 0.050 g meso gum ∴ some mistake [?] made.

The aq. filtr from the meso Ca salt evap to dryness gave xx lle crystalline Ca salts in scattering; got 2.28 g dried in vacuo which on dissolving in much cold H2O left 0.35 g insol white heavy Ca salt (? meso dioxy glutaric acid) discard & the aq. filtr evap ∴ 1.93 g Ca salts was now discarded–

<u>2nd Experiment</u>; in this case trying to first get tribasic acid, $COOH-CH_2-CH(OH)-COOH$, etc but got no better yield of the dioxy glutaric yield is about 2.0 g from 10 g Isosaccharin!

10 g Isosaccharin & 40.75 g HNO3 1.21 heated 2 days & 48 hrs from 35°–50° (mostly 35–40°) & then pour into H2O & make up to 1 L. 10 cc of this took 20.13 cc n/10 NaOH ∴ treat rest of aq. filtr with 3.6 g pure CaO in cold at first & then finally heat gently for 3 hrs at 45–50° & got 2.65 g insol $CaC_2O_4·½H_2O$; the still acid filtrate (Vol about 1½ L) was now conc in vacuo to about 100 cc & got a small amt of gummy Ca salt easily sol in cold H2O ∴ treat the aq. sol again BaCO3 1 hr with 2.0 g pure $Ca(OH)_2$ (at first in cold) & got 3.5 g insol yellow Ca salt (? air dry or ? in vacuo) & this gave 26.9 % Calcium by analysis ∴ treated rest, probably salt 3.445 g with 2.92 g oxalic 2H2O at 60° for 10 hrs & got from aq. filtr in vacuo 1.92 g gum (cont HNO3!). This gum heated in oil bath at 130° for 7 hrs gave off CO2 & finally gave back 1.45 g gum which made up with H2O to 25.0 cc & take 20 cc (∴ 6.116 g) took only 10.13 cc n/10 NaOH (6.3 cc in cold). Rest of aq. sol. treated with chinin etc took up 3.85 g chinin & gave 4.13 g (in 2 crops) diff sol in H2O chinin salts of meso & l 1,3 Dioxy glutaric acids.

The aq. filtrate from the 3.5 g insol Ca salts conc in vacuo & pptd by alcohol etc gave 6.78 g (dried in vacuo) Ca salts which contained 16.85 % Ca on analysis & treatment of the 6.5808 g Ca salts left with 3.493 g oxalic 2H2O etc gave 4.25 g gum, 50° 20 hrs, something of HNO3. This gum heated with 20 cc H2O at 130° for 7 hrs gave off CO2 & got back

(88)

Made up to 1 L with H_2O & took 25 cc (∴ 0.0975 g) &

3.9 g gum with a xx sublimate.
found 8.8 cc $\frac{n}{10}$ NaOH needed for neutralization (5.2 cc n cold) ∴ treated with 11.2 g Chinin ale
& got a total of 7.28 g diff. sol in H_2O Chinin salts in 3 crops, which with 4.13 g
obtained from yellow Ca salt makes 11.41 g Chinin salts of meso & 1,3 Dioxy glutaric acids,
[cf 1st expt which gave 12.39 g salts]. The 11.41 g treated with 7.0 g $Ba(OH)_2$ ale gave 8.42 g Chinin
+ 1.71 g gum (acetic ether ext & well swept over ex). This gum treated with 0.9 g $Ca(OH)_2$ 4 hrs BWB
gave an alk. sol. but on conc got a gummy Ca salt only which could not be handled ∴ treated
with 1.5 g oxalic 2 H_2O & got back 1.6 g gum which boiled with 8.65 g Brucin gave 11.25 g xx
salts which heated with 30 cc abs. alcohol ~~dissolved~~ easily on standing gave 4.10 g, crop I,
xxlle m.pt 120–220°. & then 1.8 g crop II m.pt 240° which looks like a mixture of 2 bodies.
These crops are probably meso & l 1,3 Dioxy glutaric

(65) Oxidation of crude l. erythro C_5 gum to Meso dioxy glutaric acid {May 14 09 / Oct 13 09 / Jan 5 10

Took the 5.3 g l erythro C_5 gum [May 14-09 No] which had stood in alcohol all summer & hydrolysed to his BWB with 30 cc H_2O, then digested K_2C etc & got back 4.9 gum with $[\alpha]_D^{20}$ = −19.8 (p = 4.167). Now divided into $\frac{9}{10}$ ths & $\frac{1}{10}$ th treated
−28° 01. i.e. found α in 1 dc tube = ... but got 24 hrs o.t. on adding ether ale a gum only ∴ neg.
latter with 0.5 cc ph hydr & 0.3 cc alcohol ... of l. erythro gum & may also contain d. threo C_5 gum but
as body is obviously a mixture of dl oxy butyrolactone and threo
not likely to any appreciable amount. Took the $\frac{9}{10}$ ths ∴ 4.5 g l erythro C_5 gum and
heated with 18.0 g HNO_3 (1.21) at 50° for 48 hrs & then pour into H_2O & make up to 1 L & take
20 cc & found 18.41 cc $\frac{n}{10}$ NaOH needed ∴ treated rest of aq. sol with 2.7 g powd CaO (2.53 g = theory)
5 hrs BWB vol 2 L & got 1.45 g insol CaC_2O_4 ½ H_2O. The aq. alkaline filtrate on evap. to a small volume
gave a separation of 0.93 g Ca salt as a heavy granular powder – obviously calcium meso 1,3 dioxy
– glutarate. This was dissolved (!) in 300 cc hot water & digested with 0.53 g $H_2C_2O_4$ 2 H_2O & got on
distilling off in vacuo & taking up residue in Acetone, besides 0.24 g insol Ca salt, 0.43 g
xxlle ~~from which got 0.2 g melting from 110–120° & losing xx H_2O at 140°~~ that slowly thrown away, obviously meso dioxy glutaric
acid (see No 66). The 0.24 g insol Ca salt (in acetone) was easily sol in cold water & on treating with
0.1 g mon oxalic etc gave 0.2 g xxlle m.pt 110–120° & losing H_2O at 140° ∴ probably a mixture of
oxalic & meso 1 3 Dioxy glutaric acids – ~~easily~~ sol in cold ether & ∴ not freely & slowly
considered to be mesotonic acid. (N.B. dl Malic may be present in the meso Ca salt) (cf Vellis, No 45)
The aq. filtrates from 0.93 g meso Ca salt gave on pptg with alc ale 4.55 g air dry Ca salts
or 3.9 g meso dried Ca salts containing 18.15 % Ca ∴ treat rest of anhydr. salt with 2.18 g oxalic 2 H_2O
& got 2.55 g mobile gum (Acetone ext). This digested with Chinin took up 8.55 g & gave a total
of 4.74 g (diff. sol in H_2O) 2 crops Chinin salt. The 4.74 g salts gave with 5.0 g $Ba(OH)_2$ ale 3.7 g Chinin
+ 0.53 g gum (acetone ext) which with 2.9 g Brucin etc gave 3.4 g xx salts which warmed with 30 cc
abs. alcohol left 1.05 g insol Brucin salt m.pt 223° (? dl Mal ic Brucin): this on xx from 2 cc
H_2O & 20 cc alcohol gave xx prisms of dl Malic Brucin & heavy opaque nodules of meso 1,3 cont. meso 1 3 Dioxy glutaric
Dioxy glutaric Brucin

(89)

(66°) The oxidation of d erythro C_5 gum to meso 1,3 dioxyglutaric acid. May 19 - 10

Took 16,35 g Brucin salt m.pt 198°-200° $[\alpha]^{20}_D$ = -23°,2 of 4,96 g hydrated Brucin salt of c.p. d. erythro C_5 Brucin $[\alpha]^{20}_D$ = -21°,81 (May 2 - 10) & got c. 8,0 g $BaOH_2$ etc 16,02 g Brucin and 4,82 g c.p. d. erythro C_5 gum (alc xtr). This gum on heating 36 hrs at 45 - 50° with 20 g HNO_3 1,21 & then add H_2O & make up to 1/2 L. 10 cc took 18,73 cc $\frac{n}{10}$ NaOH ∴ treated rest of aq. sol with 3,5 g pow'd $CaCO_3$ 3 hrs B_wB got 1,94 g mesol CaC_2O_4 & H_2O contain trace $CaCO_3$ & a yellowish Ca salt [most boiled this out long time B_wB with 1 L H_2O & treated for aq. pptd CO_2 etc got on evap. practically nothing ∴ no meso Ca salt possibly present]. On conc. the alkaline aq. filtrate to a small volume got 0,74 g (in 2 crops) of a (heavy) xx Ca salt which took about 1 L water on B_wB to dissolve (∴ a very diff sol. salt): the solution was sat. CO_2 & then boiled etc & filtrate then conc. on B_wB gave on conc. to a small volume (?) anhydrous Calcium mesodioxyglutarate 0,5 g as a heavy xx salt which lost nothing on drying over H_2SO_4 in vacuo. These were now treated with 700 cc H_2O (not all in solution) & then 0,290 g oxalic $2H_2O$ added & the mixture digested & shook long time to ensure complete saturation to CaC_2O_4 etc. Then distill off aq. filtrate in vacuo & take up R.T. in moist Ether (1 L) & got on conc this to a small volume 0,16 g + 0,02 g meso 1,3 dioxy glutaric acid (and lactone acid) in the form of transparent tabular often cubical xxlle m.pt 120-130° losing H_2O & ptly solid & then not melting until 170° melting point of meso lactone acid (Kiliani 168)

0,1789 g acid gave 0,2563 g CO_2 & 0,0763 g H_2O

	Found
Theory for $C_5H_8O_6$ 36,59 / 4,88	for $C_5H_6O_5$ 41,10 / 4,11	39,07 / 4,74

∴ about eq. pts free acid & lactone acid

It took Kiliani over 20 years to get the lactone acid;

The aq. filtr from 0,74 g meso Ca salt on ppting with alc etc gave 4,23 g vacuo dried Ca salts containing 23,16 % CaO ∴ treat rest 4,0875 g partly insol in H_2O ∴ gum meso salt present with 2,130 g oxalic & got on treating aq. filtr with 11,0 g Chinin etc. A total of 6,12 g diff sol in H_2O Chinin salts which gave with 3,0 g $BaOH_2$ etc 4,86 g Chinin & 0,53 g gum (HNO_3 noticed in dist off ∴ chinin tartrate present) easily sol in a small amt of cold ether & probably a mixture of various acids (& discard).

(67) Oxidation of a mixture of eq. amts l. threo & d. erythro C_5 gums from l. Xylose etc Jan 3'10

Took the 6,0 g mixed C_5 lactone gums [April 8-09 No. 35] called l. threo C_5 gum [not proved later see Nos 69 & 70 to be a mixture of l. threo & d. erythro C_5 gums] & mixed with 24,3 g HNO_3 (1.21) & heated to 50° for 48 hrs & then add H_2O & make up to 1 L & take 10 cc & used 12,18 cc $\frac{n}{10}$ Na treated rest of aq. sol treated with 3,50 g pow'd CaO (4 hrs B_wB) gave 2.08 g CaC_2O_4 & aq. filtrate evap to a small volume gave no diff sol Ca salts ∴ pptd by alc etc & got 6,52 g vacuo dried Ca salts containing 17,3 % Ca on analysis ∴ treat rest of salts 6,3387 g with 3,45 g oxalic $2H_2O$ & distill off in vacuo 70° 25 min (HNO_3 noticed in d.f.) on taking up residue in warm acetone etc got 3.35 g gum (mobile & smelling faintly of HNO_3) This took up 11,55 g Chinin & gave, in all,

a total of 7.35 grs (dif f. sol in H_2O) Cinchonin salts which with 5.0 g $Ba(OH)_2$ alc gave 6.1 g Cinchonin & 1.07 g gum (acetone extr). These gave with 5.8 g Brucin alc 7.15 g xx salts from xx these from 20 cc absol. alcohol got 4.48 g crop I salts mpt 120–220°; then crop xx from 3 cc H_2O + 75 cc alc (it don't dissolve in absol alc) gave 2 kinds of xx ll ∴ probably a mixture of meso + d 1,3 dioxy glutaric Brucin. discard all material at this point

(68) l Arabinose + 33% NaOH final. Oct 7 09 Dec 28 09 Jan 22–10 Feb 19–10 Mch 15–10

251 g 99% NaOH in 418 cc H_2O (2 l flask) (t 40°) & add quickly shaking a hot sol of 100 g l. Arabinose, mpt. 150–160° in 200 cc H_2O & rinse with 50 cc H_2O & then heat quickly putting in $BaSO_4$ H_2O trap cord ete 8 hrs & then cool, dilute & add 1123 g 20.16% HCl (theory 1115 g) & then distill off in vacuo & ext c alcohol & got 80 g gum. This dissolved in 110 cc H_2O & ext 20 x by ether gave 22.9 g ether sol C_3 C_4 gums and 57 g gum (left in H_2O which ext 2 x 1 x with 400 & 1 x with 200 cc Ethylacetate left a small amt of wood tar & NaCl (total 19.4 g)). got from ethylacetate solutions & evaporating over 1 X with H_2O 37.7 g gum; acylated this 9 hrs 115 cc anhydr 100° & got 59.45 g acylated gums of which all dissolved except 3.6 g tar (discard) in shaking with cold ether. add to ether sol. also the acylated gums obtained from 22.9 C_3 C_4 gums (see below) & got a total of 56.5 g acylated gums (from ether sol) which hydr 2 x c H_2O 3 pts gave 36.7 g I & 35.7 g II & then with 90 g $Ba(OH)_2$ & 250 cc H_2O 8 hrs 100° alc gave 33.45 g C_3 C_4 C_5 gums. The 22.9 g gum ext from H_2O sol by ether as stated above were shaken in cold 2 x with 200 cc ether & 1 X with 100 cc Ether dissolving each time & found 2.6 g wood tarry gum left which acylated with 8 cc Essiganhydr 9 hrs 100° & got 3.8 g ether sol acylated gums waste (see above) and 1.1 g insoluble tar (discard). got back from cold ether solutions 18.5 g C_3 C_4 gums S I & 8.3 g more ether soluble C_3 C_4 gums S II. The 33.45 g gums was dissolved in 67 cc H_2O & ext 20 x by ether gave 8.3 g gum in cold with 20 cc ether and lead left in H_2O solution 25.4 g C_5 gums; shook the 8.3 g gum in cold with 20 cc ether and all except 1.1 g by diff dissolved add to 25.4 g lot & det acc as 26.7 g C_5 gums $[\alpha]^{20}_D = 24.5$ ($p = 4.0$) gave ... C_3 C_4 gums left in cold ether gave 6.95 g II with

$[\alpha]^{20}_D$ ($p = 4.0$) $= -8.28$ ∴ 20% C_5 gums still present & titration of $\frac{1}{25}$th ∴ 0.278 g took a total of 28.15 cc $\frac{n}{10}$ NaOH (16 cc in cold). The 18.5 g C_3 C_4 gums I treat with H_2O & KnC in $BaSO_4$, distill off in vacuo & take up in alcohol etc gave back 16.6 g gum which gave $[\alpha]^{20}_D = -5.19$ (∴ 16% C_5 gums still present) & titration of $\frac{1}{50}$th (∴ 0.332 g) took total of 31.95 cc $\frac{n}{10}$ NaOH (10.5 cc in cold). Now combine aq. solutions of C_3 C_4 gums from ether sol I and II & distill off in vacuo & dissolve gums (about 22.9 g) in 50 cc H_2O & ext 20 x with Ether & got from ether sol gums after treating with H_2O KnC ether 14.65 g C_3 C_4 gums $[\alpha]^{20}_D = -2.47$ ($p = 4.0$) & titration of $\frac{1}{50}$ th ∴ 0.293 g took total of 30.58 cc $\frac{n}{10}$ NaOH ($12\frac{1}{2}$ cc in cold) ∴ treat rest of aq. sol. with 58.0 g Brucin (theory 59.0 g) etc & got 79.4 g xx salts which xx from 100 cc absol. alcohol seeding with dl 1,3 dioxy butyric Brucin gave 19.2 g crop I salts mpt 185–188° $[\alpha]^{20}_D = -29.76$ ($p = 4.0$) and then got from filtr 56.8 g salts which dissolved in 70 cc alcohol alc gave 17.44 g crop II mpt 185–187° $[\alpha]^{20}_D$ ($p = 4.0$) $= -29.96$.
Now got back 34.6 g gummy salts which xx from 50 cc absol. alcohol gave 10.5 g crop III dl lactic Brucin mpt 200–205°. The alc. filtr from crop III gave 23 g salts which with 12.0 g $Ba(OH)_2$ etc. gave 15.5 g Brucin and 2.78 g & (5.70 g) gum which was resolved by digestion with 0.5 L ether into 2.78 g gum $[\alpha]_D = -9.15$ insoluble with 4.8 g below & 1.13 g gum which was treated with ... $[\alpha]^{20}_D = -9.15$. The 5.7 g gum (see p 91) into by 100 cc ethylacetate R.T. into 1.13 g C_3 gums 14.08 g crop I
20 g Brucin etc gave 26.6 g xx salts which xx from 60 cc absol. alcohol gave rapidly 10.7 g salts 1,3 dioxybutyric Brucin mpt 185–188° $[\alpha]^{20}_D = -30.63$ ($p = 4.00$). The alc. filtr. gave back 1.68 g gum [hot ether extr R.T. 1.48 g united with 2.78 g above ...] which by 5.0 g $Ba(OH)_2$ alc gave 7.25 g Brucin and 1.68 g gum & on shaking this in cold with 50 cc ether all but 0.2 g gum dissolved & latter which was united with 0.22 g ∴ 0.45 g C_5 gums which with 1.13 g above made 1.58 g C_5 gum S.

See p. 92

removed by ether etc.

(after a 14,65 g gum $[\alpha]_D^{20} = -2,47$ had been
20 x
The aq. solution left ~~after extracted with ether gave~~ 6,95 g C_4 C_5 gums $[\alpha]_D^{20} = -14°84$ ($p = 4.0$)
A
was forcibly treated with Chinin (took up 20 g) but gave no xx from alcohol no xxlle of d. threo
C_5 Chinin ∴ united alc. filtrate with a corresp. filtrate obtained from other C_5-gum st
the 26,7 g C_5 gums (see p 90) found ($p = 4.0$) to be $[\alpha]_D^{20} = -24°,5$; titration taking two ths ∴ 0.267 g
took 21.26 cc $\frac{n}{10}$ NaOH ($2\frac{1}{2}$ cc in cold) + theory for C_5-lactone = 20.22 cc. Now treat all of gum with 68,2 g
Chinin 9 hrs BWB + got 3,31 g insol. Chinin + from aq. filter got 109.9 g xx salts which xx from 116 cc
alcohol gave 28.39 g d. threo C_5 Chinin m.p. 172°, crop I, ; the alc. filtr gave 73,5 g salts which xx
from 140 cc alcohol gave only 2,6 g more xxlle m.p. 153–160° crop II. The alc. filtrate from crop II
was now combined with alc solution of Chinin salts obtained from 6,95 g ($-14°84$) gum above
[16,95 g + 5,7 g]
+ got back with 45 g $Ba(OH)_2$ etc 58,15 g air dry Chinin + 3x ether, SO_4" etc gave ^ gum which was resolved by shaking
with cold ether into 5.7 g C_3 C_4 gums $[\alpha]_D^{20} = -9°,15$ (see p. 90) + titration of $\frac{1}{25}$th ∴ 0.228 g took
which when extr R.7. with 0,5 L ether took up 7,45 g mobile gum [illegible]. Extraction of gum left insol. in 1st 0.5 L
22,06 cc $\frac{n}{10}$ NaOH (11 cc in cold); and into 2.05 g C_5 gums. Extraction of gum just mentioned gave a total of
ether R.7. with alcohol etc + including the 2,05 g C_5-gum just mentioned gave a total of
16.95 g C_5 gums $[\alpha]_D^{20} = -18°55$ ($p = 4.0$) ; titration of $\frac{1}{50}$th ∴ 0.339 g gave 26.43 cc $\frac{n}{10}$ NaOH theory
(for C_5 lactone = 25,7 cc) ∴ treat rest of aq. sol. with 49,6 g Brucin etc got 74 g xx salts which
xx from 100 cc alcohol gave 22.2 g crop I l. erythro C_5 Brucin m.p. 165°–172° too cryst. 46,15 g salts
obtained from alc. filtrate got 20.25 g crop II l. erythro C_5 Brucin m.p. 175–177° + then could get no
more xxlle ∴ set free gum by 10 g $Ba(OH)_2$ + got 15,53 g Brucin + 6,6 g black gum (alc extr)
which was ∴ ~~extr~~ acylated 8 hrs 100–110° with 20 cc anhyd. + got 10,8 g acylated gums of which 2.0 g tar
remained insol on extr with ether + got from ether extracts on 1st hydr. (H_2O 3 pts 8 hrs 100–H_2O) 5,65 g + then by
15 g $Ba(OH)_2$ + 50 cc H_2O 8 hrs BWB etc got back 5.25 g C_5 gum which took up in H_2O 7 hrs BWB
11,8 g Chinin + gave 22,45 g xx salts which on xx from 40 cc alcohol gave only 1.4 g more d. threo C_5
Chinin m.p. 172° + got from alc filtr distilled off in vacuo 17.4 g salts rexx these from 40 cc alc more d threo
salt ∴ set free gum by 10 g $Ba(OH)_2$ + got 10,83 g Chinin + 4,35 g C_5-gum (cont tar) ∴ acylated
with 14 cc anhyd. 8 hrs 100° + got 6.9 g acylated gums + removed 0,9 g tar remained insol on extr c ether
+ got on hydrolysis of ether sol. gums 1X with H_2O → 3,95 g + then with 10 g $Ba(OH)_2$ + 25 cc H_2O + got
3,05 g C_5 gum (acetic ether extr + 1X sweep wr.) with $[\alpha]_D^{20} = -9°,52$ ($p = 4.0$). Now distill off H_2O +
extr gum R.7. 2X with 300 cc ether each time + got 1,0 g insoluble clear, almost colorless, gum
(100° vacuo) which was found $p = 4.0$ to be absolutely inactive optically + titration of $\frac{8}{25}$ ths
∴ 0,32 g took only a total of 20,83 cc $\frac{n}{10}$ NaOH theory for C_6 lactone = 19.76 cc
" " C_5 lactone = 24,24 cc

∴ conclude that some synthetic C_5 + C_6 gums must be formed in traces from the
combination of Diose + Triose + Hexose molecules with each other Q. E. D.

The rest of the C_5 gum extr by ether 2,05 g which must now be $[\alpha]_D^{20} = -12°5$
was now discarded.

Now had (see bottom p. 90) following unidentified gums left only

ether sol. gums 2,78 g + 1,48 g united ; and 1,13 g + 0,45 g C_3-gums united not sol. in cold ether.

The acc. det. of ether sol. gums now gave 4,34 g gum + titration of $\frac{15}{250}$ ths (i.e. 0,2604 g) gave

26.99 cc $\frac{n}{10}$ NaOH ∴ treated rest of aq. sol. with 16.6 g Brucin + got (1x sweep over c alc) 21.9 g xx salts

which xx from 50 cc alcohol gave 5.1 g crop I 1,3 Dioxy butyric Brucin m.pt. 185°–190° & then

got 3.77 g crop II m.pt 188°–205° obviously a mixture of lactic + 1,3 Dioxy butyric Brucin.

The alc. filt. from crop I gave no more xxlle ∴ set free gum by 6.0 g $Ba(OH)_2$ + got 8.29 g Brucin +

1,24 g gum (ether extr) sol in 6 cc cold ether ∴ treated it with 1,0 g $ZnCO_3$ 7 hrs B_2O_3 + got 0.26 g mod. alc. / dl Znlactate xxlle crop I only. aq. filtr

$ZnCO_3$ + from aq. filtr adding alc etc got a total of 0,67 g

gave gummy zinc salts only ∴ mix tures of C_4 salts ∴ discard.

1,3 Dioxy butyric lactone: Now took the various fractions of 1,3 Dioxy butyric Brucin as follows: 19,2 g $[\alpha]_D^{20} = -29°{,}76$ and

14,08 g $[\alpha]_D^{20} = -30°{,}63$; 17.74 g $[\alpha]_D^{20} = -29°{,}46$ ∴ total used = 50,72 g [? and free Brucin and dl lactic Brucin xx]

extr C_6H_6 + add SO_4 etc 39.0 g rec. dry Brucin and 9.72 g gum (ether extr) a

l. erythro & Brucin). Got with 25.0 g $Ba(OH)_2$ etc

mobile acid smelling gum ; on shaking this in cold with 50 cc ether got a resolution into

5,62 g ether sol. gum – (see below) C_4 erythro gum present (16% or more) ; this gum treated with

and into 4,13 g ether insol gum $[\alpha]_D^{20} = -5°{,}93$ ∴ 1,3 Dioxy butyric ph. hydrazide ; got after

4 cc ph. hydr + 4 cc alc got o.t. entirely solid with xxlle of 1,3 Dioxy butyric ph. hydrazide

standing 40 hrs o.t. + add water alc etc till snow white 3,0 g 1,3 took 0, 6935 g xx and 16,6855 g H_2O ∴ p =

m.pt. 128°–130° where $[\alpha]_D^{20}$ p = 4.0 absolutely 0,0° i.e. Q.E.D. Keep rest of prep.

d = 1011 at + found α in 2 dc tube = absolutely ± 0,0°

The 5,62 g ether sol gum heated 7 hrs B_2O_3 with 4,0 g $ZnCO_3$ etc gave 1,01 g insol $ZnCO_3$ &

got from aq. filtr on conc adding alc etc a total of 0.47 g xx dl lactate of zinc ~~only~~ in 1st crop.

" " " 0,58 g dl lactate of zinc in 2nd crop.

3,5 g gum (ether extr). On treating this with 4 cc ph. hydr

Now pptd zinc in aq. de filtrate by H_2S etc and got

2,5 g snow white 1,3 Dioxy butyric phenyl hydrazide

+ 4 cc alcohol o.t. 44 hrs seeding etc got

m.pt 130° (Keep) Q.E.D.

dl lactic acid. The 10,5 g dl. lactic Brucin obtained, crop III, m.pt. 206°–208° (see p. 90) gave with 5.0 g $Ba(OH)_2$

extr 3x C_6H_6 etc SO_4 " 8.29 g Brucin and 1,76 g lactic acid gum sol in cold ether. Now took also the 5.1 g

and 3.77 g crops of Brucin salts (see above) m.pt 190°–205° ∴ mixtures of 1,3 Dioxy butyric + lactic + got by 5.2 g

$Ba(OH)_2$ etc extr 3x C_6H_6 SO_4 etc 6.67 g Brucin & 1,54 g gum sol in 5 pts cold ether ∴ united with 1,76 g

lot ∴ total = 3,3 g gum & this boiled with H_2O + 2,5 g $ZnCO_3$ 7 hrs. B_2O_3 gave 0,63 g insol $ZnCO_3$

aq. filtr conc + add alc. etc gave a total of 3,03 g xx crop dl lactate of Zn 3 H_2O corresp. to 1.8 g dl lactic acid ; rest gave only gummy

zinc salts ∴ discard –

d. threo & Chinin; Had a total of 29.78 g salts (in 2 crops) 1.4 + 28.39 g ; on xx these from 240 cc absol alcohol (R.T.) got

20,45 g crop I d. threo salt m.pt 172° $[\alpha]_D = 103°{,}3$ i.e. took 0,9027 g subst and 21,6452 g H_2O ∴ p = 4,002 &

found α in 1 dc tube = $-4°{,}18$. The alc. filtr gave back 9,5 g salts to which were now added 2,6 g more

of low melting crude d. threo salt m.pt 155°–160° crop II p 91 and on xx these from 40 cc alcohol got 4,6 g

more cp. d. threo C_5 salt m.pt 172°. discard alc filtr containing about 7,5 g salts only obviously

simply carried down mechanically by porous character of d. threo salt.

Now took the 25,05 g cp. d. threo salt in 2 crops 20,45 + 4,6 g + got with

12,0 g $Ba(OH)_2$ etc 17 g Chinin and 6,93 g (alc extr) mobile

colorless d. threo C_5 gum $[\alpha]_D^{20} = -36°{,}5$ (p = 4,0) α in 2 dc tube = $-2°{,}95$.

6.93g)

Now make gums with H_2O up to 500cc & take 100cc ∴ 1.386g lactone substd of H_2O in excess & treat gum with 1.4cc ph. hydr. 87.4cc alcohol 95% 24 hrs, shaking, & adding acetic after till snow white 1.6g ph. hydrazine kept 75–85° while xx from 80cc hot alcohol after gave 0.87g snow white hydrazide mpt 108°–110° with $[\alpha]_D^{20} = +26°36$ i.e. 0.4635g subst and 11.0865g H_2O ∴ p = 4.015 and found α in 1dc tube = +1°07.

analysis: 0.2065g subst. gave 0.4170g CO_2 and 0.1253g H_2O

	Theory for $C_{11}H_{16}N_2O_4$	Found
C	55.00	55.05
H	6.67	6.74

Rotation Na salt: took 50cc ∴ 0.693g lactone gum and 52.5cc $\frac{N}{10}$ NaOH by titr. & distill H_2O in vacuo & dissolve Na salt, 0.9028g by theory, in H_2O to make total weight = 21.570g (∴ p = 4.18) and found α in 2dc tube = +2°01 hence $[\alpha]_D^{20} = +23°76$

use rest of cop. gum 4.851g for oxid expt see No 61

The l. erythro C_5 gum: lead salts of 42.45g Brucin salts in 2 crops 20.25 & 22.2 which obviously consisted of a mixture of dl. 1,3 Dioxy butyric Brucin & l. erythro C_5 Brucin whose separation was exceedingly difficult. The xx of the 42.45g salts from 300cc alcohol got 31.2g crop I, salts mpt 170°–172° with $[\alpha]_D^{20} = -36°5$ :: obviously much free Brucin present with salts; the alc filtrate from crop I gave 11.2g salts which xx from 30cc alcohol gave 5.02g crop II mpt 160°–170° & alc. filtrate from crop II gave 5.8g Brucin salts soluble in H_2O giving a neutral or very slightly alkaline reaction after heating on $BaCO_3$ in H_2O solution ∴ discard this part as probably being lactic Brucin.

Now work the crops I & II Brucin salt 31.2 & 5.02g salts = 36.22g dissolved in about 250cc cold H_2O extr 5x by C_6H_6 & proved that 2.35g mpt 175–178 Brucin in C_6H_6 extr destilling off H_2O from aq. filtrate got back 41.5g xx salts which xx from 50cc alcohol gave 0 because too much H_2O present ∴ distill off 50cc at 25mm & got 43.15g salts which on xx from 50cc alcohol & then on standing a large amt of heavy white granular crystals ∴ add 5cc more alcohol & then filter & got 25.95g crop I mpt depr 170–180° which was obviously a mixture of l. erythro C_5 Brucin and dl 1,3 Dioxy butyric Brucin, and perhaps also some dl. lactic acid ∴ treat this with 13.0g $BaCl_2$ & then C_6H_6 & then dry ether & got 18.85g Brucin and 5.42 soluble gum (Ether extr) with $[\alpha]_D^{20} = -28°03$ (p = 4.0) i.e. found α in 2dc tube = −2°29 ∴ about 75% l. erythro C_5 gum being considered pure l. erythro gum & oxid by HNO_3 (Nos. 65 &), the alc. filt from crop I above gave 8.4g salts which gave very little xx from 30cc alcohol etc ∴ & free gum by 5.0g $BaCl_2$ etc got 4.54g Brucin & 2.1g gum (ether extr) with $[\alpha]_D^{20} = -23°87$ (p = 4.0 ∴ total 7.52g α in 2dc tube = −1°93 ∴ unite the 2 crude erythro C_5 gums 5.42g and 2.1g and on getting rid of H_2O in vacuo & dissolving in 15cc H_2O extr 20 by ether got from aq. sol 3.249g C_5 gum (90° 25mm) with $[\alpha]_D^{20} = -32°4$ (p = 4.0) and from ether solution got 4.25g soluble and smelling gum which was now shaken in cold with 50cc ether and got in cold ether 1.22g gum with $[\alpha]_D^{20} = -14°22$ (p = 4.0) i.e. found α in 2dc tube = −1°15 (p = 4.0) ∴ discard. The portion insol in 50cc cold ether was 2.8g gum with $[\alpha]_D^{20} = -25°84$ p = 4.0 ∴ it is certain that this was 60% C_5 l. erythro gum besides the 3.249g which was about 80% l. erythro C_5 gum.

The 3.29 g gum $[\alpha]^{20}_{D} = -32°.4$ was digested with with H_2O & 8.1 g Chinine 7 hrs Bath & got
17.15 g XX salts (after 2x sweep over c alcohol ale) & this XX from 30 cc alcohol gave 2.0 g, crop I, crude
d. threo C_5 Chinin mpt. 160°–165°, & then no more XXlle from alcohol.
Similarly the 2.8 g gum $[\alpha]^{20}_{D} = -25°.84$ gave on digestion with 6.9 g Chinin ale (1x sweep over c alc)
11.85 g salts which XX from 25 cc alc gave 1.85 g crude d. threo C_5 Chinin mpt 150–153° & then got 9.25
g salts which XX from 20 cc alcohol gave 2.46 g crop II crude d. threo C_5 Chinin a mpt 150–155°.
The combined alcoholic filtrates from the d. threo salts (both lots) about 17.65 g Chinin salts
gave back with 10.0 g $Ba(OH)_2$ ale 8.92 Chinin & 3.0 g gum (lost ether extr) $[\alpha]^{20}_{D} = -27°.84$ (p = 4.0)
which on shaking in cold with 50 cc ether was resolved into
0.87 g ether sol gum $[\alpha]^{20}_{D} = -21°.51$ (p = 4.0) ~~and~~ α in 1 dc tube = −0°.87
into 2.01 g insol gum $[\alpha]^{20}_{D} = -31°.9$ (p = 4.0) α in 1 dc tube = −1°.29
The 2.01 g gum was warmed gently with 163.46 cc $\frac{n}{10}$ NaOH & sol. remained very faintly alkaline &
on dist. off H_2O in vacuo & dissolved Na salt 2.663 g, by theory, with H_2O so as to make total weight =
66.575 g (∴ p = 4.0) and found α in 1 dc tube = −0°.20 hence $[\alpha]^{20}_{D} = -4°.95$ which proves
that ~~only~~ much l. erythro C_5 gum ~~can~~ must be present as rotation of d. threo Na salt ~~must be~~ is +23°.76
~~over +12° $[\alpha]^{20}_{D}$ [calculate from Brucin salt $[\alpha]^{20}_{D}$ = −18°.77 as~~ see p 93 ∴ Therefore set free gum
again from Na salt by 163.5 cc $\frac{n}{10}$ HCl ale & got back 1.84 g l. erythro gum which with 5.4 g
Brucin ale gave 8.54 g XX Brucin salts which XX from 100 cc abs. alcohol gave large amt of
transparent flat square plates (and sm. amt of flour needles) mpt 170°, crop I, 2.87 g
sale. filtrate gave 4.75 g salts which XX from 10 cc alcohol gave rapidly XX prisms 3.17 g crop II Brucin
salt mpt 180–183° which XX again from 30 cc alcohol gave 2.46 g XXlle mpt 180–182° $[\alpha]^{20}_{D}$ =
−27°.67 0.9461 g & 22.8404 g H_2O ∴ p = 3.977 & found α in 2 dc tube = −2°.22. → −30°.72 i.e.
crop I 2.87 g similarly reXX from 15 cc alcohol gave 2.61 g XXlle mpt 170° with $[\alpha]^{20}_{D}$
0.9798 g salt and 23.6631 g H_2O ∴ p = 3.984 & found α in 2 dc tube = −2°.47.
Therefore obviously l. erythro C_5 Brucin mainly containing in ~~last case~~ some d. threo salt ~~; some free Brucin~~.
The 0.87 g gum $[\alpha]^{20}_{D} = -21°.51$ gave with 75.6 cc $\frac{n}{10}$ NaOH a faintly alk. permanent sol. on warming & on dist off H_2O in
vacuo & dissolved Na salt, 1.172 g by theory, in H_2O to total weight = 29.30 g (∴ p = 4.0) found α in 1 dc
tube = −0°.20 ∴ $[\alpha]^{20}_{D} = -4°.95$!! ∴ obviously l. erythro C_5 gum present. Now set free gum by
75.6 cc $\frac{n}{10}$ HCl ale & got back 0.87 g gum which with 2.5 g Brucin ale gave 3.87 g XX salts & these
XX from 5 cc alcohol slowly gave transparent flat plates & prisms 1.69 g crop I mpt 180–186° ~~with~~
XX from reXX this again from 20 cc abs. alcohol got 1.36 g mpt 180–188° with $[\alpha]^{20}_{D} = -29°.9$
~~$[\alpha]^{20}_{D}$ =~~ i.e. 0.9167 g salt & 21.9699 g H_2O (∴ p = 4.004) & found [α] in 2 dc tube = −2°.42 ∴ body was
~~almost pure~~ crude l. erythro C_5 Brucin. The orig. ale filtr from crop I gave 1.72 g salts which XX from
4.5 cc alcohol gave rapidly 1.03 g XX prisms crop II mpt 185° & these XX from 10 cc alcohol then
gave 0.79 g XXlle mpt 182–184° $[\alpha]^{20}_{D} = -30°.2$ ∴ mainly l. erythro C_5 Brucin
The three crops of crude d. threo C_5 Chinin salts mentioned on top p. 94 2.0 g + 1.85 g + 2.46 g in all ∴ 6.31 g
were now reXX from 40 cc alcohol and got only 2.42 g salt mpt 160° & this XX from
15 cc alcohol gave 1.26 g Chinin salt mpt 165° ∴ still impure d. threo Salt
∴ unite all salts 6.31 g again & got with 4.0 g $Ba(OH)_2$ ale
4.12 g Chinin + 1.58 g gum (Ether ext)

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which 1.58g was now treated with 4.7g Brucin & gave 7.08g xx salts and these xx from 10cc absol alcohol gave 2.85g crop I mpt 160°–170° (plates & porous needles) these when re xx from 20cc hot alcohol gave 2.52g heavy coarse grouped nodules made up of plates with pointed ends mpt 160°–165° with $[\alpha]_D^{20} = -29°.08$ ∴ nearly l. erythro C_5 Brucin i.e. 0.9200g salt and 22.0975g H_2O (∴ $p = 3.996$) & found α in 2dc tube = −2°.35.

Moving alc. filtrate from crop I above gave 3.4g salts & these xx from 10cc alcohol gave 2.52g, crop II, mpt 170–175° & this xx from 20cc hot absol. alcohol gave 2.04g heavy coarse grouped xx nodules made up of prisms, mpt 170°, with $[\alpha]_D^{20} = -23°36$ ∴ obviously a mixture of about eq. amt. d. threo & l. erythro C_5 Brucin salts. Q.E.D.

Noticed now that the d. threo C_5 Brucin $[\alpha]_D^{20} = -18°.77$, from March 15 09, had only 0.28g xx from 3.5cc hot absol. alcohol & gave 0.23g heavy xx nodules somewhat opaque & melting at 160° it also xx in transp tabular xx lle see March 15 '09 – [∴ Kelp] [cf No 34 p 44

Now unite all Brucin salts described on pp 94–95 as follows 2.52g ($[\alpha]_D^{20} = -29°08$); 2.04g (−23°36); 1.36g (−29°.9) 2.46g ($-27.67 = [\alpha]_D^{20}$); 2.61g ($[\alpha]_D^{20}$ −30°72) ∴ 11.74g salts, alc mother liquors cont in all a total of 16.6g Brucin salts.

Found on further trial it was impossible to get pure l. erythro C_5 Brucin which should melt up to 200°; but on uniting all salts & heating in H_2O solution to combine all gum again with Brucin and then distilling off in vacuo 50° only at 25 mm & xx the salts obtained from 5cc H_2O & 50cc alcohol & scratch – as in case of separation of d. erythro & l. threo gums from l. Xylose (see No 69) got 1st crop of xx ~~lle~~ 4.04g mpt 170°–175°, with $[\alpha]_D^{20} = -29°82$ and then on distilling off alc. at 50° and 25 mm got 12.0g salts which xx from 20cc absol. alcohol gave 5.43g, crop II, salts mpt 180°–183° with $[\alpha]_D^{20} = -33°53$ ∴ some free Brucin present.

Crop I, 4.04g gave with 2.0g $Ba(OH)_2$ 2.73g ~~Brucin~~ & 0.92g stiff C_5 gum, which treated with 2.25g Chinin & H_2O & ext. aq. sol 3x with ether & distill off H_2O in vacuo gave 3.4g xx salts easily soluble in 10cc absol. alcohol & nothing comes out on standing ∴ l. erythro C_5 Chinin must be very sol. in alcohol – in marked contrast to the d. erythro salt (see No 69) ∴ can separate d l erythro easily into optical components by means of Chinine Q.E.D.

The 5.43g crop II gave with 2.5g $Ba(OH)_2$ etc 3.99 Brucin & 1.3g stiff C_5 gum which treated with H_2O & 3.19g Chinin $BaSO_4$ & then when cold ext 3x with ether etc gave 4.5g xx Chinin salts which were easily soluble in 10cc absol. alcohol & gave nothing on standing & scratching ∴ l. erythro C_5 Chinin is very soluble in alcohol – Q.E.D.

Now get back gum from each lot by $Ba(OH)_2$ etc & got back 0.95g gum and 0.75g gum as sep. (but ether extrs). The smaller amt 0.75g gave with 0.8cc ph. hyd & 0.8cc alcohol 0.7.38 hrs a solid mass of xx lle or after adding acetic ether stirring etc washing finally with ether got (in vacuo) 0.95g l. erythro C_5 ph. hydrazid mpt 145°–150° !!

The larger lot 0.95g treated with 1.0cc ph. hydr. & 1cc alcohol did not give any xxlls after 16 hrs. st. ∴ seed with xxlls of other & got 38 hrs st. 0.50g ph. hydr. of l. erythro C_5 gum m.pt 140–145° ∴ combine with 0.85g of the 0.95g lot (from using 0.1g of 0.95g lot for dl body) the xx 1.35g of the crude erythro ph. hyd. from 20 cc absol alcohol got very rapidly a large amt of snow white conc. grouped needles: after 5 hrs standing add 25cc ethyl acetate, filter & wash first with ethyl acetate & finally with Ether & got 0.96g cp. l. erythro phenyl hydrazide m.pt 150° with $[\alpha]^{20}_D = -8.93$ i.e. 0.3844g substance and 9.2555g H_2O ($p = 3.987$) and found α in 1 dc tube $= -0.36°$

Analysis: 0.1987g subst. gave 0.4042g CO_2 and 0.1236g H_2O
0.2101g " gave 22.3cc dry N_2 at 22°.2 and 730.1 mm

Theory for $C_{11}H_{16}N_2O_4$		Found
C	55.00	55.50
H	6.67	6.91
N	11.67	11.85

dl. phenyl hydrazid of C_5 erythro gum; made from 0.1g l. erythro C_5 ph. hydr. m.pt 145°–150° and from 0.1g recd d. erythro C_5 ph. hydrazid (No 69 April 16–10) from rotation expt. mixed & dissolved these in 2cc hot absol. alcohol (mixture noticeably more soluble than either component) & scratch & soon got xxlls; after 5 hrs add 5cc ethyl acetate, filter & wash 1st with ethyl acetate & finally with ether & got 0.15g dl body m.pt 130° ∴ not a real racemate

Q.E.D. [Keep] –

(69) l. Xylose and 33% NaOH. {Oct 8.09 Dec 29 09 Jan 22–10 (2 places) Feb 22–10 Feb 26–10 March 17–10 April 16–10 May 2 –10

251g 99% NaOH in 413cc H_2O at 40° (2 l. flask) & add quickly hot sol. of 100g l. Xylose m.pt 150° in 200cc H_2O then rinse with 50cc H_2O & then put at once in boiling WB H_2O kept constant over [illegible] 8 hrs & then pour into 1124g 20.16% HCl (theory 1115g) etc & distill [illegible]: take up salt residue in alcohol & got 88g gum which dissolved in 110cc H_2O & ext. 20 by ether gave 29.9g ether sol. C_3C_4 gums I and got from H_2O sol 56.5g gum which on drying 1x c400cc & 1x with 200cc ethyl acetate left 15.63g mostly NaCl but traces of tar only. Got from ethyl acetate sols (100° vacuo) 42.85g gums which dissolved in 40cc alc & add 120cc ether & shake was resolved into 33.75g soluble gum B and into 8.7g ppted dark stiff tarry gum C (acylate this see below). Gum B dissolved in 60cc H_2O & ext. 20x by ether gave 11.6g ether sol C_3C_4 gums II and lead left in H_2O solution 21.25g gums B acylated this and sim. amts from C_3C_4 gums I & II see below.

C_3C_4 gums I 29.9g shaken in cold with 400cc ether, decant & then shake again with 100cc more ether left 2.1g mostly gum ppt with B 21.25g lot and acylate. C_3C_4 gums II 11.6g shaken in cold with 200cc ether 2x left 1.8g mostly gum which was like urse added to B 21.25g & acylated.

Unite the cold ether extracts of the C_3C_4 gums & det accurately as 35.2g.

On acylating gum B 21.25g + 2.1g + 1.8g as indicated with 75cc acetic anhydr 9 hrs 100° got 41.05g acylated gums of which 20g tar (discarded), remained insoluble on ext with cold ether stirring.

Acylation of gum C 8.7g with 27cc anhydr 9 hrs 100° gave 13.7g acylated gums of which 1.9g brown tar remained insol in ext with ether etc. Unite the acylated gums of B & C & got a total of 49.6g acylated gums which on 2x hydr. (c H_2SO_4 to 8 hrs WB 120°) gave 31.1g & 30.8g gum syrup & then on hydr with 70g $Ba(OH)_2$ & 200cc H_2O (8 hrs WB) finally got

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(from 100 g l. Xylose.

29,35 g C_5 gums, which with 35,2 g C_3 C_4 gums about make a total of 64,55 g Saccharins)

The 35,2 g C_3 C_4 gums shaken in cold with 0.5 L ether left 6,0 g gum insoluble see dist with vacuo this gum after dissolving in H_2O, treating KnC, taking up in alc after dist off H_2O in vacuo was found to weigh 5,5 g, have $[\alpha]_D^{20}$ (p = 4.0) = +19°4 & titration of $\frac{15}{250}$ (∴ 0,33 g) took 31,63 cc $\frac{n}{10}$ NaOH (theory for C_4 lactone = 32,36 cc) ∴ dissolved rest of recovered gum, 5,1 g, in 11 cc H_2O + ext 20 by ether and had left in H_2O solution 2.2 g C_5 gums $[\alpha]_D^{20}$ = +22°,58 (p = 3,98) whereas ether sol portion, 2.9 g by diff, was added to 26.15 g left C_3 C_4 gums (see below)

The C_3 C_4 gums dissolving in the 0,5 L. cold ether was now digested in H_2O sol. with KnC & filtered, distilled off H_2O in vacuo, take up residue in alc etc & got back 26,15 g C_3 C_4 gums with $[\alpha]_D^{20}$ = +6°,8 (p = 4.0) & got by titration of $\frac{1}{100}$ th (∴ 0,2615 g) a total of 26.79 cc $\frac{n}{10}$ NaOH (10.5 cc in cold)

Now distill off H_2O from rest of gum and add to it the 2.9 g taken out by ether as stated above and dissolved combined gum (about 28 g) in 60 cc H_2O & ext 20 x with ether and got a resolution into 18.7 g ether sol. C_3 C_4 gums with $[\alpha]_D^{20}$ = +3°9 (p = 4.0) and into 8.35 g C_5 gums $[\alpha]$ = +16°7 (p = 4.0) which made with 2.2 g C_5 $[\alpha]_D^{20}$ = +22°58

therefore makes 10,55 g C_5 gums I and 29.35 g C_5 gums II

The 29.35 g C_5 gums II gave $[\alpha]_D^{20}$ = +25°73 (p = 4.0) & titration of $\frac{1}{100}$ th (∴ 0,2935 g) took 23.88 cc $\frac{n}{10}$ NaOH (theory for C_5 lactone = 22.23 cc) ∴ treated rest of aq. sol. with 76,6 g Chinin 7 hrs BWB & had 2,38 g wool thin & got 135 g xx salts which dissolved in 135 cc alcohol gave 16,55 g crop I of l. threo d. erythro C_5 Chinin (about 60 g) mpt 165°; the alc. filtr der. distilled off gave 98,5 g salts which xx from 200 cc alcohol gave 29.85 g crop II mpt 160° l. threo d. erythro C_5 Chinine and then no more ∴ unite alc. filtr from C_5 gums I.

The 10,55 g C_5 gums I gave with 25 g Chinin BWB etc a total of 38,55 g salts & on xx these from 50 cc alcohol got 6,75 g, crop I, l. threo d. erythro C_5 Chinin mpt 160° & then no more ∴ unite alcoholic filtrate about 30 g with corresp. alc. filter from C_5 gums II & got with 50.– grs $Ba(OH)_2$ & got 61,65 g Chinin & ext 3 x ether & add sep alc 22,35 grs (7.95 g + 14.45 g) gum which was ext R.T. with 0.5 L ether

Taking out 9.95 g mobile gum, of which on shaking 2 x in cold with 100 cc ether a total of 7.95 g was dist dissolved with $[\alpha]_D^{20}$ = +5°44 (p = 4.0) titration of $\frac{10}{250}$ th ∴ 0.318 g took 32.1 cc $\frac{n}{10}$ NaOH (19.5 cc in cold) C_3 C_4 gums

Got finally also, from insoluble portions (alc ext) a total of 14.45 g C_5 gums with $[\alpha]_D^{20}$ = +21°76 (p = 4.0) and titration of $\frac{1}{50}$ th (∴ 0.289) took total of 23.11 cc $\frac{n}{10}$ NaOH (5.3 cc in cold) (theory for C_5 lactone = 21.70 cc).

Decided at this point (stupidly) to treat rest of aq. sol 14.161 g gum with 42,5 g Brucin and got 65.0 g salts which xx from 100 cc alcohol gave (cont → cps. p) 10,53 g crop I salts mpt 150°–165° & then from alc filt got 48,35 g salts which xx from alc 100 cc gave 18.1 g crop II salts mpt 175°–177° and then got from alc filtrate 27.85 g salts which xx from 50 cc alc gave 3,19 g crop III mpt 170–74°. The alc. filtr gave 23.35 g salts which ~~xx from~~ gave with 10.0 g $Ba(OH)_2$ etc 15.9 g Brucin and 6.2 g brown gum which was acylated 3 hrs 100–10° with 20 cc anhydride & got 10.05 g acylated gums of which 1.75 g tar remained insoluble on ext with Ether etc. Hydrolysis of the sol acylated gums gave I c H_2O 5,6 g & then with 15 g $Ba(OH)_2$ & 50 cc H_2O 8½ hrs BWB got back 5,0 g C_5 gums & this treated

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with 12.0 g Chinin ale gave 20.55 g xx Salts which on xx from 30 cc alcohol only gave 1.25 g l threo d. erythro C5 Chinin mpt. 165°, crop I; + then 1.48 g crop II mpt 153°–160° + then 2.05 g crop III mpt 155°–160°.

The alc. filtr from crop III now gave with 7.0 g $Ba(OH)_2$ alc 8.08 g Chinin + 3.6 g gum tarry ∴ acetylated it 9 hrs 100–110° with 11 cc acetyl Cl + got 0.87 g tar + 4.55 g ether. sol acetylated gum which on hydr 1 x c H_2O gave 2.95 g gum + then with 10 g $Ba(OH)_2$ + 25 cc H_2O 8 hrs 100° gave 2.4 g gum with $[\alpha]^{20}_D = +13°.1$ ($p = 4.0$). alc extr then gave R.7. 2 x with 300 cc ether had left 0.73 g non mobile stuff almost colorless gum with $[\alpha]^{20}_D = +11.0$ ($p = 4.0$) ∴ discarded but obviously may consist of traces synthetic C_5 gums besides l. threo + d. erythro C_5 gums.

C_3 C_4 gums

Had 18.7 g I $[\alpha]^{20}_D = +3°.9$ and 7.95 g II $[\alpha]^{20}_D = +5°.44$.

18.7 g lot, take $\frac{15}{1000}$ th pt ∴ 0.2805 g of gum ∴ 30.56 cc $\frac{n}{10}$ NaOH needed (26 cc in cold) ∴ treat rest of aq. sol with 78.0 g Brucin + got xx of 106 g salts from 130 cc alc 17.87 g, crop I, mpt 185–188° with $[\alpha]^{20}_D = -29°.68$ ($p = 4.0$) then got 88 g salts which xx from 100 cc alcohol gave 23.95 g crop II mpt 185–187° with $[\alpha]^{20}_D = -30°.16$ ($p = 4.0$) and then got 54 g salts which xx from 70 cc alc gave 19.05 g crop III mpt 207–9° ∴ dl. lactic Brucin + finally got 34 g Brucin salts which with 18.0 g $Ba(OH)_2$ alc. gave 22.7 g Brucin and 5.4 g C_3 gum which 4.3 g easily dissolved in 100 cc cold ether + rest 1.1 g C_4 gums remained insoluble (unite with corresp gums from 7.95 g lot as stated below)

7.95 g lot treat with 30 g Brucin gave 37.35 g salts which xx from 80 cc alcohol gave 14.45 g, crop I $[\alpha]^{20}_D = -29°.4$ ($p = 4.0$) ∴ mainly 1,3 Droxy butyric Brucin + then no more ∴ set free gum from rest of salts by $Ba(OH)_2$ + got 11.8 g Brucin and 2.95 g gum [~~the R.7.~~] which was resolved into 2.6 g C_3 C_4 gums soluble easily in 50 cc cold ether and into 0.35 g C_5 gums less soluble ∴ unite these with corresp. lots from 18.7 g lot 4.3 g + 1.1 g + ∴ have 6.9 g C_3 C_4 gums unidentified and 1.45 g C_5 gums: the latter after digestion KCN alc gave back 1.38 g gum with $[\alpha]^{20}_D = +14°.6$ ($p = 4.0$) : there is evidently smaller present as gum is too stiff for a pure C_5 gum ∴ discarded.

→ titration of this lot acc dat as 6.82 g gum taking $\frac{10}{250}$ ∴ 0.2728 g a total of 28.14 cc $\frac{n}{10}$ NaOH ∴ treated rest of aq. sol. with 26.5 g Brucin + got 36.9 g xx salts (1 x sweep over c alc) + got by loss in 70 cc alcohol 5.52 g crop I salts mpt 185–180° ∴ mainly 13 Droxy butyric Brucin: had a spill thro' flask cracking in scratching crop I but got back 24.25 g Brucin salts which on xx from 30 cc alc gave 5.05 g crop II mpt 180–203° ∴ mixture lactic + 1,3 Droxy butyric Brucin. The alc. filtr from crop II gave 18.35 g salts which xx from 25 cc alcohol was giving a fair amt of cubes of dl lactic Brucin but decided now to set free gum from all of the 18.35 g salts by 9.0 g $Ba(OH)_2$ alc + got 12.58 g Brucin and 2.62 g gum easily sol in 12 cc cold ether. The gum was ∴ digested with 2.0 g $ZnCO_3$ 3 hrs $BaCO_3$ stuff 0.54 g insol $ZnCO_3$ + got on conc. aq. filtr + adding alcohol alc a total of 1.73 dl lactate Zn 3 H_2O x x lle besides some gummy zinc salts ∴ a mixture of much lactic + some 1,Oxy butyrolactone.

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1,3 Dioxybutyric acid; took the following crops of 1,3 Dioxybutyric Brucin (p 98)
19,45 g ($[\alpha]_D^{20}$ = −29°4); 17,87 g (−29°68); 23,95 g (−30°6); ∴ total = 61,27 g: these gave with 30 g $Ba(OH)_2$ etc
48,53 g Brucin and 10,93 g gum (ether extr) which latter was resolved by shaking in cold with 50 cc
ether into (a) 7,0 g soluble + sharp smelling dl lactic gum cont 1 oxybutyrolactone and into
(b) 4,04 g insol 1 oxybutyrolactone gum $[\alpha]_D^{20}$ = +4°45 (p = 4.0) ∴ some d sugar gum present.
The 4,04 g gum (b) treated with 4 cc ph. hydr + 4 cc alcohol gave o.t. after 40 hrs standing seeding + washing etc
2,87 g 1,3 Dioxybutyric ph. hydr m.pt 128°–130° with $[\alpha]_D^{20}$ = −0°37 (p = 4.0) i.e. took 0.6738 g +
16,166 g H_2O ∴ p = + found α in 2 dc tube = −0°03 (5 readings). Keep rest of prep ∴ pract ±
The 7,0 g (a) gum treated thus with 5 g $ZnCO_3$ left 1,23 g insol $ZnCO_3$ + got on conc aq. filtr etc by alc
a total of 2,88 g dl Zn lactate 3 H_2O (one crop) + from aq. alc. filtr by H_2S etc got back 4,1 g gum, ether extr
This gave with 4,5 cc ph. hydr + 4 cc alc o.t. 44 hrs etc 3,2 g 1,3 Dioxybutyric ph. hydrazid m.pt
130°–2° (Keep) Q.E.D.

dl. lactic Brucin, crop III, 19,05 g (p 98) m.pt 207–209° gave with 10 g $Ba(OH)_2$ etc 15,22 g Brucin and
3,25 g dl lactic gum (cold ether extr) + this on treating thus with 2,5 g $ZnCO_3$ thus left 0,46 g insol $ZnCO_3$
+ gave in all in one crop 4,11 g** dl lactate of Zn 3 H_2O (corresp to 2.5 g dl lactic gum).

The other 2 crops of Brucin salts on p 98 5,05 g m.pt 188°–205° and 5,52 g m.pt 185–190° gave with 5,0 g $Ba(OH)_2$
8,11 g Brucin and about 2,0 g gum easily sol in ether lost by accident (but of comp. fractions
from l. lactamide) + undoubtedly a mixture of lactic + 1 oxybutyrolactone –

The C_4 gums; the Chinin salt coming out from alcohol, m.pt 165° with $[\alpha]_D^{20}$ = −113° or so, was
long supposed to be a definite acid – but it proves to be a mixture of eq. pts. l. threo +
d erythro C_4 gums – whose subseq. separation by Brucin is exceedingly difficult.
Had a total of 55,88 g Chinin salts in 5 crops (29,85 g + 16,55 g + 6,75 g + 1,25 g + 1,48 g): these were
now xx from 450 cc absol. alcohol and got a separation of 40,50 g crop I m.pt. 166° with
$[\alpha]_D^{20}$ = −113°2 i.e. 0,9047 g and 21.6973 g H_2O (∴ p = 4.003) gave α in 1 dc tube = −4°58.
The alc. filtrate from crop I salts gave back 17.0 g salts + these xx from 50 cc alcohol gave 6,04 g
l. threo d. erythro salt m.pt 160–5° (Keep) whereas the alc filtrate which still contained 12.9 g salts
was found (after evaporating in vacuo etc) to give an alkaline reaction + give much free Chinin insol in H_2O ∴ it was discarded.
The 40,50 g crop I l. threo d. erythro Chinin salt treated with 20,0 g $Ba(OH)_2$ etc gave 27,72 g Chinin and
10,7 g mobile C_4 gums with $[\alpha]_D^{20}$ = +39°56 (p = 4.0). This gum was now made up to 1 L with H_2O +
take 100 cc (∴ 1,07 g) for ph. hydrazine test after removing H_2O in vacuo etc + then treating with 1,1 cc ph hydr +
1,1 cc alc but could get no xx hydrazide by scratching by addition of ether or of acetic ether ∴ n.g.
2nd Expt took 60 cc of aq. solution ∴ 0.642 g gum and treated with 48,64 cc $\frac{n}{10}$ NaOH = theory for C_4 lactone
+ found the pract. neutral solution after distilling off H_2O in vacuo + making up Na salt 0.8364 g
$C_5H_9O_5Na$ by theory to total weight 20.91 g (∴ p = 4.0) and found α in

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2 dc tube was $-0^\circ.26$ hence $[\alpha]^{20}_D = -3^\circ.15$. According to calculation l. threo C_5 Na should give $[\alpha]^{20}_D = -23^\circ.76$ and d. erythro C_5 Na should give $[\alpha]^{20}_D = +15$ to $+20^\circ$ ∴ about eq. amts of 2 gums must be present – a conclusion also reached from rotation of mixed Chinin salt Q.E.D.

Now got back gum l. threo d. erythro from rest of aq. sol (840 cc).

The xx Brucin salts obtained from the 14.45 g C_5 gum s $[\alpha]^{20}_D = +21^\circ.76$ p. 97 bottom

Had a total of 31.84 g salts in 3 crops (18.1 + 10.55 g + 3.19) & supposed for a long time time to be the d. erythro C_5 gum whereas the diff. sol. Chinin salt was considered to be the salt of the l. threo C_5 gum which is N.G. as proved later. It is obvious that these salts represent mixtures of Brucin salt of l. threo d. erythro C_5 gum with more or less 1,3 Dioxy dl butyric present.

The xx the 31.93 g salts from 200 cc alcohol got 21.25 g crop I mpt 170°–172° with $[\alpha]^{20}_D (p = 4.0) = -30^\circ.5$; got from filtrate on xx from 30 cc alc 5.81 g crop II mpt 160°–170° (sol. filtr was discarded). Now dissolved crops I & II salts in about 150 cc cold H_2O & extr 5x with C_6H_6 which removed by acc. alc

1.73 g Brucin mpt 175–178° from distilling off H_2O in vacuo got 29.7 g xx salts which xx from 50 cc alc gave 0 as too much H_2O present but on distilling alc again in vacuo & warming gently salts, 28.45 g with 50 cc alcohol not all would dissolve but bear much insol micro xx powder ∴ heat on B.W.B. & then till almost dissolved & on cooling got large amount of heavy thin flat plates with pointed ends 18.8 g crop I mpt 170–175° crop I gave with 10 g $Ba(OH)_2$ alc 13.25 g Brucin and 3.93 g gum [Ether extr] with $[\alpha]^{20}_D = +20^\circ.4$ (p = 4.0) ∴ clearly a mixture of about eq parts C_4 & C_5 gums – The alc. filtrate from crop I had 7.45 g salts which with 5.0 g $Ba(OH)_2$ alc gave 3.9 g Brucin and 1.72 g gum (Ether Extr) with $[\alpha]^{20}_D = +29^\circ.67$!!

Now took of similar fractions of so called d. erythro C_5 Brucin from l. Xylose expt No 35 p. 50 of June 22–09 3.0 g salt $[\alpha]^{20}_D = -26^\circ.85$ 192° $[\alpha]^{20}_D = -25^\circ.64$ and 1.61 g salt mpt 185–190° Took 3.07 g salt mpt 194° $[\alpha]^{20}_D = -25^\circ.1$ and 1.16 g for rotation) and 5.84 g mpt 185–190° which treated with 5.0 g $Ba(OH)_2$ alc & got 13.75 g salts (1x sweep over with alc) mpt 170°–177 (from 4.1 g having used 1.16 g for xx) & extr 5x with C_6H_6 & got 1,3 Dioxy butyric Brucin. ∴ total amt = 13.52 g. Now dissolve these in H_2O & extr 5x with 185°–190° which xx from 130 cc alcohol gave 9.24 g xx alc filt discarded (Ether extr) $[\alpha]^{20}_D (p = 4.0) = +9^\circ.77$ ∴ mainly 1,3 Dioxy butyric Brucin.

gave 6.3 g Brucin & 1.7 g gum

The 1.7 g gum was ∴ heated in open dish c H_2O for 8 hrs and weight went down to 1.05 g & gum got brown in color and its $[\alpha]^{20}_D$ went up to $+14^\circ.1$ (p = 4.0); this also shows that C_5 gums are carried off in traces with 1 Oxy butyrolactone –

The 3.93 g gum $[\alpha]^{20}_D = +20^\circ.4$; the 1.05 g $[\alpha]^{20}_D = +14^\circ.84$; the 3.93 g gum $[\alpha]^{20}_D = +20^\circ.4$

Now unite gums as above lines as follows; the 1.05 g $[\alpha]^{20}_D = +14^\circ.84$; the 3.93 g gum which however had also been warm in open dish B.W.B. with H_2O for 6 hrs & had lost weight going down to 3.41 g and the 1.72 g gum $[\alpha]^{20}_D = +29^\circ.67$. Therefore total combined gums is 6.18: Shook this in cold with 60 cc Ether and found 1.0 g gum $[\alpha]^{20}_D = +10^\circ.88$ p = 4.0 had dissolved

The rest of the gum left workable 5.1 g whose $[\alpha]^{20}_D$ was at least $+25^\circ$ was seed treated with 12.5 g Chinin & got 1x sweep over with alc alc 22.48 xx salts which xx from 45 cc alcohol gave 8.77 g crop I l. threo d. erythro C_5 Chinin mpt 160°–2 with l. threo obviously predominating by what follows!

and then got 2.08 g crop II salt m.pt 150°–155°. Unite these ∴ 10.85 g + xx from 65 cc absol alc
and got 6.46 g l. threo d. erythro Chinin m.pt 163°–5 with $[\alpha]_D^{20} = -115^\circ 3$ $p = 4.0$ ∴ l. threo predominates
↓ alc. filtr discarded.
The orig alc. filtrate from crop I + II threo erythro Chinin gave back 7.7 g salts which with 5.0 g BaOH –
alc gave 4.53 g Chinin + 1.51 g gum (ether extr) with $[\alpha]_D^{20} = +15^\circ 57$ ($p = 4.0$) ∴ united
this with 1.0 g gum $[\alpha]_D^{20} = +10^\circ 88$ see p 100 near bottom ∴ 2.5 g unidentified gum & shook
this in cold with 50 cc ether & resolved it thus into 1.14 g ether sol gum $[\alpha]_D^{20} = +6^\circ 18$ ($p = 4.0$)
and into 1.35 g insol gum $[\alpha]_D^{20} = +19^\circ 53$ ($4.0 = p$). The 1.14 g lac treated with 10.8 cc $\frac{n}{10}$ NaOH
gave a faintly alk. sol after warming + on dist. off H_2O in vacuo + making up Na salt 1.572 g by theory
to total weight $p = 4.0$ ∴ for calc gs with H_2O found α in 1 dc tube was $-0^\circ 087$ whence $[\alpha]_D^{20} = -2^\circ 15$
Similarly the 1.35 g gum treated with 117.3 cc $\frac{n}{10}$ NaOH till just faintly but perm. alkaline when warm sol
gave on dist off H_2O + making up Na salt, 1.819 g by theory, with H_2O to gs total weight (∴ $p = 4.0$)
gave $[\alpha]$ in a 1 dc tube $= -0^\circ 293$ whence $[\alpha]_D^{20} = -7^\circ 25$. These results simply prove that
l. threo C_5 Na salt is present in slightly larger ratio than d. erythro C_5 Na L of p 100 top.

Proof that the Chinine salt m.pt 166° $[\alpha]_D^{20} = -113^\circ 2$ + its resulting gum 10.7 g p. 99 bottom
was a mixture of eq. pts l. threo + d erythro C_5 metasaccharinic acids –

(Had 7.918 g l. threo d. erythro gum left from the 10.7 g gum (i.e. used 260 cc for expts of the 1 L sol), the
last 100 cc being used with Brucin Jan 22-10 + is not described in detail here.
↓ Then used also 3.5 g l. threo d. erythro gum obtained from various sources of d. threo l. erythro
Chinin m.pt 163°–166° eg. the 6.46 g above; 3.32 g obt from xx of 6.04 g crude salt
m.pt 160°–165° Dec 29-09; also 2.33 g + 1.33 g eq. l threo d erythro salt May 12 09
∴ got in all about 11.4 g l. threo d. erythro C_5 gum, for separation into components.
These were now treated with 34.0 g Brucin. Gave 52 g xx Brucin salts. (see top next page)

11.4

A prelim expt with 1.07 g d. threo d. erythro gum + ~~4.3~~ 3.0 g Brucin had established that get a resolution of 4.3 g xx salts by ~~10 cc alc~~
into crude d erythro C_5 Brucin by xx from 10 cc alcohol as 1st crop obtained by xx from 10 cc absol. alc gave
2.96 g xx m.pt 185°–190° & these when rexx from 70 cc alc. gave 1.42 g xx previous m.pt 185°–190° with
$[\alpha]_D^{20} = -25^\circ 64$ ($p = 4.013$). Subsequently noticed that this salt comes out very slowly but completely from alc cont
~~[struck]~~ H_2O & that m.pt goes up to 202° or higher and $[\alpha]_D^{20}$ goes down to $-22^\circ 75$ or even lower. The
l. threo salt is not carried down to as large extent under these conditions as when absol alcohol alone
is used when simply always get mixed xxlle of the salts of the 2 acids – even at
first resolution (a quant is exceedingly diff & has not yet been accomplished tho' both products have been obtained pure –

The 11.4g d.erythro l.threo ~~~ gave with 34g Brucin alc 5.2g salts which dissolved in 60cc alcohol +let slowly (seeding with crude d.erythro Brucin mpt 185–193° $[\alpha]_D^{20} = -25.64$) gave 21.62g salts mpt 160°–180° ∴ a mixture; the alc. filtr gave 28.0g salts which xx from 100cc hot abs. alcohol gave 11.88g crop II salts mpt 185–192° ∴ mainly d.erythro salt.

crop I rexx from 300cc alcohol gave 6.94 salts mpt 180°–190° and then 5.24g salts mpt 185–187°.

After much work got thus a separation into 23.78g (a) salts melting from 180°–194° and into an alcoholic filtrate containing 18.65g (b) gummy easily sol. in alcohol salts.

The former (a) ~~also~~ could not be got pure by repeated xx from alcohol large or small amts & is a mixture of much d.erythro salt containing l.threo salt in varying proportions.

Now took (a) 23.78g salts, dissolve in H_2O, extr 5x C_6H_6 (to remove supposed excess of Brucin) alc +got distilling off H_2O at 50° only at 25mm +got 26.05g salts which dissolved in 75cc alcohol gave ~~1st bulky opaque nodules in large amts + then on top of these got transp. xx prisms~~ 1st transp. heavy xx prisms in large amts then slowly on top of these got opaque bulky nodules which were dissolved easily on gentle warming; got 7.65g xx prisms mpt. 190°–200° – obviously mainly d.erythro C_5 Brucin;

On xx this from 4.5cc H_2O and 50cc alcohol this gave 5.72g d.erythro C_5 Brucin mpt 202°–3° with $[\alpha]_D^{20} = -22°71$; i.e. 0.8321g salt and 20.0404g H_2O ∴ $p = 3.987$ +found α in 2dc tube $= -1°83$.

It is doubtful if this is cp. d.erythro Brucin – but conc ~~use this~~ got the pure erythro from from this with Chinin (or better still probably by conversion into the phen. hydrazide). Now set free gum from all of 5.72g d.erythro salt by 3.0g $Ba(OH)_2$ +got 4.15g Brucin and 1.18g gum (that after extr) with $[\alpha]_D^{20} = +54°8$ ($p = 4.0$) (α in 1dc tube 2°22). N.B. a small amt of the C_5 gum is always left insol in ether +sol in acetone, alc or acetic ether +this is less + hence got $[\alpha]_D^{20}$ usually about +40°.

The 1.18g +54°8 gum gave with 2.89g Chinin alc 4.65g xx Chinin salt which is very diff sol. in abs alcohol + comes out very completely on cooling: the 4.65g salt aq. took 80cc hot alcohol to dissolve even hot on standing got crop I 3.05g xx needles mpt 172° with $[\alpha]_D^{20} = -104.°0$ i.e. 1.0119g and 24.3090g H_2O (∴ $p =$ 3.996) gave α in 1dc tube $= -4°20$; the salt can also be xx from a small amt of H_2O. The alc. filtrate from 3.05g crop I gave on conc 0.43g more crop II same salt ∴ 172° ∴ write.c (see p 103)

Now took (b) 18.65g salts added Brucin extr by C_6H_6 from (a) above to it, heated in H_2O solution, cool +extr 5x C_6H_6 etc +got distilling off H_2O only at 50° at 25mm 21.35g xx salts which xx from 50cc alcohol slowly gave opaque bulky xx nodules, 10.94g, crop I mpt 150°–160° (loses xx H_2O); on xx these from 5.5cc H_2O +60cc alcohol got slowly conc. grouped flat prisms, 4.62g, mpt 145°–150° crop I l.threo C_5 Brucin with $[\alpha]_D^{20} = -34°07$ unite this with 1.33g salt $[\alpha]_D^{20} = -33°47$ +working up for l.threo gum (see p. 103). The alc. filtr from crop I l.threo salt gave on conc alc 3.0g xx alc mpt 145°–150° with $[\alpha]_D^{20} = -27°80$ ∴ a mixture of l.threo + d.erythro (eq. pts).

The orig. alc. filtr from crop I, 10.94g above gave on distilling off alcohol sirupy salts (about 11g) in 20cc alcohol, 3.43g xx nodules mpt 170–183° ∴ mixture.

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{3,6 g C_5 guM ether extr
{2,1 g C_5 guM (sticky) alc extr

Without going into further details the Brucin salts (a) and (b) were separated further by xx various fractions acc. to mpt., opt. rotation etc., into 6,78 g crude d. erythro Brucin mpt 190°–202° and into another 1,33 g xx fraction, l. threo salt mpt 145–150° $[\alpha]^{20}_D = -33°47$ whereas rest still remained mixtures of 2 salts in question (these gave with 10,0 g Ba(OH)₂ alc 14.9 g Br... 3,6 g ... ether extr ... 4,1 ... α 33°07 & the 1,33 g + (pp 102–103) and last ether extr 1,11 g l. threo C_5 guM; Now took the 2 fractions of l. threo salt, 4,24 g Brucin and 3.0 g $Ba(OH)_2$ total = 5,95 g salts; got with 3,034 in 2 dc tube α –33°47 ∴ (p = 4.0) (N.B. trace of C_5 gums not extr by ether in all cases)
l. threo gum $[\alpha]^{20}_D = +42°5$ + got 4,85 g xx Chinin salt (l threo) which xx from 30 cc alcohol with 2,72 g Chinin [too low as salt still not absol. free from d. erythro].
Now treated the 1,11 g gum with crop I 2,14 g xx needles, mpt. 160°–2° with $[\alpha]^{20}_D = -119°45$ gave α in 1 dc tube = –4°84; the alc. filtr. dist off xx from i.e. 0,960 g subst and 22,9890 g H_2O (∴ p = 4007) gave crop II mpt 160°–2° ∴ unite. N.B. the Chinin salt of l. threo gum is noticeably more soluble in alcohol than d. threo salt and especially also the d. erythro Chinin salt ∴ thought could sep 10 cc alc. gave 0,50 g from l. xylose but n.g. (see below).
d. erythro C_5 gum II: the 6,78 g crude erythro Brucin salt 1st & 3rd fr. mpt 190°–202° gave with 3,0 g $Ba(OH)_2$ 4,92 g Brucin and 1,4 g d. erythro gum & this with 3,4 g Chinin this Bu. extr 3x ether we gave 4,75 g xx salts which xx from 70 cc alcohol gave a total of 3,33 g ? d. erythro Chinin mpt 179° with $[\alpha]^{20}_D = -105°7$ i.e. 0,9191 g salt and 29,8874 g H_2O (∴ p = 2,983 too much H_2O by mistake) d = 1,00 ... found α in 1 dc tube = –3°,8. 3,48 3,80
The alc. filtrate dist off & xx from 10 cc alcohol gave 0,47 g more Chinin salt mpt 171°
Now took the various d. erythro Chinin salts as follows 3,33 g + 0,47 g + 3,05 g + 0,43 g (p 102) ∴ about 7,0 g & treat with 3,0 g $Ba(OH)_2$ alc & got 4,95 g Chinin and 1,93 g d. erythro gum (alc extr); now divided this into 2/3 and 1/3 and used 1/3 for ph. hyd + 2/3 for Brucin salt [see]
ph hydrazide 1/3 of the 1,93 g gum heated with 0,65 cc ph. hydr + 0,6 cc alcohol quickly gave xx needles on stand. r.t.; after 24 hrs add acetic ether, filter & wash well & got 0,88 g mpt 140–145° very diff sol in ethyl acetate even on boiling ∴ best use alcohol for r xx. xx the 0,88 g from 10 cc absol. alcohol & got rapidly transparent cone grouped slender needles in large amts. Before filtering add 10 cc ethyl acetate (room temp), shake & then filter & wash c. cold ethyl acetate – got 0,68 g cp. d. erythro C_5 ph. hydrazide snow white mpt 150° with $[\alpha]^{20}_D = +9°38$ i.e. 0,3971 g subst and 9,6477 g H_2O (∴ p = 3,955) and found [α] in 1 dc tube = +0375. recd ph. hyd from aq. sol. (used 0.1 g for dl ph hyd (see No 68 p

analysis 0,2076 g subst. gave 0,4202 g CO_2 and 0,1272 g H_2O

	Theory for $C_{11}H_{16}N_2O_4$	Found
C	55,00	55,20
H	6,67	6,81

l. threo C_5 gum continued: took the 2,64 g l. threo C_5 Chinin salt & got with 1,2 g $Ba(OH)_2$ alc 1,85 g Chinin and 0,8 g gum (alc extr); this with 0,8 cc ph. hydr + 0,8 cc alcohol got entirely solid in 20 hrs r.t. after 24 hrs add acetic ether, stir, filter & wash & got 1,1 g crude hydrazide mpt 100°–110°. This xx from ~~100~~ 90 cc last acetic ether gave 0,79 g cp. ph. hyd mpt 110–120° as a snow white, very bulky ppt. $[\alpha]^{20}_D = -25°44$, i.e. 0,3721 g subst and 9,0081 g H_2O ∴ p = 3,966 gave α in

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got back pl hyd + (Keep)

1 dc tube = $-1°{,}02$.

<u>Analysis.</u>

0.1953 g subst gave 0.3948 g CO_2 and 0.1186 g H_2O

0.2069 g " gave 21.6 cbcm dry N_2 at 22°25 and 730 mm

Theory for $C_{11}H_{16}N_2O_4$ — Found

	Theory	Found
C	53.00	55.12
H	6.67	6.76
N	11.67	11.65

Took 0.1 g of above c.p. l. threo ph hyd + 0.1 g rec'd c.p. d threo ph hyd & dissolved in small H_2O & evap in desicc in vacuo & powder, then ×× it from 1 cc absol alc & got a solid cake of bulky needles; added 5 cc ethyl acetate & filtered & got 0.14 g ××lle mpt 128–130° (Keep) ∴ not racemate.

see — softening before begin at 120° ∴ — melts 130° with softening

dl threo C_5 ph. hydrazide (mpt 130°) see No. 68 p.

<u>d. erythro C_5 Brucin</u> (cont from p. 103) Took the 2/3 of 1.93 g gum & treated Ba ss with 3.8 g Brucin ext'r 3× C_6H_6 & dist off H_2O in vacuo & got 5.4 g ×× salt which ×× from 1.2 cc H_2O + 25 cc alcohol gave very slowly transparent cone grouped 4 sided flat prisms in large amts, which gradually grew to very heavy opaque nodules; got 4 days o.t. 3.65 g ××lle mpt 170° with ×× H_2O off & gets solid & then melts towards 200° again. The salt loses ×× water very slowly and in small amounts & incompletely at 100°–105° & in trying to drive ×× H_2O off by heating higher 135–140° found that slight decomposition took place! ∴ can't remove ×× H_2O. The slightly decomposed salt was ∴ re×× ~~from 2.17 cc H_2O + 20 cc alcohol~~, after adding 2.17 g of a similar dry hydrated salt (−23°05 $[\alpha]^{20}_D$) obtained later ~~in~~ from 2 cc H_2O + 20 cc alcohol and got 4.96 g salt mpt 200°–202° with previous softening at 170° showing that main portion of salt had been converted into the anhydrous salt by this process; the salt, 4.96 g gave $[\alpha]^{20}_D = -21°83$ p = 4012 i.e. 1.0131 g salt and 24.2482 g H_2O and found α in 2 dc tube = $-1°{,}77$.

Now used all this lot 4.96 g for oxid. to meso dioxy glutaric acid see No 66 p. 89.

<u>Non identified C_5 gums</u>; as mentioned on p. 103 top, got from rest of Brucin salts by $Ba(OH)_2$ etc 3.6 g C_5 gums (ether extr) and 2.6 g C_5 gums (alc extr). As it was at first thought it might be possible to separate d. erythro + l. threo C_5 gums – owing to diff in sol. of their Chinin salts in alcohol – it was necessary to prove that this is an impossibility. Accordingly foll. expts were carried out. The 3.6 g lot took in H_2O sol 8.8 g Chinin & after 3× ext c ether etc got 12.85 g salts which ×× from 70 cc absol. alc. gave 6.7 g crop I l threo d. erythro Chinin mpt 162–4° $[\alpha]^{20}_D = -111°8$ (p = 4.0); on re×× this from 90 cc absol alc seeding with c.p. d erythro Chinin $[\alpha]^{20}_D = -104°0$ got 4.68 g crop I l. threo d. erythro Chinin mpt 165–170° which again ×× from 1 cc H_2O + 20 cc alcohol gave 3.21 g ××lle mpt 168°–170° $[\alpha]^{20}_D = -111°5$ ∴ Can't separate l threo from d. erythro Chinin Q.E.D.

The orig. alc. filtrate from crop I, 6.7 g salts, gave 5.0 g salts which ×× from 15 cc alcohol gave $[\alpha]^{20}_D = -111°9$. gave 8.25 g salts; got from 50 cc alcohol 2.34 g ×× crop I

2.04 g crop II mpt. 160°, $[\alpha]^{20}_D$ ... with 6.5 g Chinin etc 3× ether

dodo. on treating the 2.6 g gum with 6.5 g Chinin etc 3× ether ... 2.22 g crop II $[\alpha]^{20}_D = -108°5$ mpt 160°

mpt 160°–2° with $[\alpha]^{20}_D = -109°1$ and then 2.22 g crop II ... started with 4.0 g

Finally took a total of 8.0 g Chinin salts whose $[\alpha]^{20}_D$ ranged from 107°4 to 113°2 & started with 4.0 g ... 5.23 g Chinin + 2.26 g C_5 gums; these treated with 6.75 g Brucin etc gave 9.55 g ×× salts

$Ba(OH)_2$ etc & got 5.23 g Chinin

which xx from 40 cc absol. alcohol gave 3.75 g salts, crop I, m.pt 160°; ~~190~~ gets solid & then melts 195–200° ∴ mainly hydrated d. erythro Cs Brucin as $[\alpha]^{20}_D$ found to be −23°.05.

Got back also 2.95 g gum from easily sol. Chinin salts left in filtrate & these with 8.85 g Brucin extr 3× C_2H_5 alc gave 11.5 g salts which xx from 20 cc alcohol gave 4.0 g xx lle m.pt 160° & these when xx from 1 cc H_2O + 20 cc alc gave 1.39 g crude l. threo Brucin xx lle m.pt 155°–157° with $[\alpha]^{20}_D$ = −31°.96.

As a final outcome stopped when had a total of about 16.4 g Brucin salts not yet identified i.e. resolved into fairly pure l. threo or d. erythro salt as shown by m.pt & polariscope — these were ∴ added to Brucin salts made from a new lot of l. threo d. erythro gum see No 70

(70) l. Xylose & 33% NaOH May 19–1910

2 lots of 100 g l. Xylose m.pt 150–5° each acc to 69 (initial temp +50° next temp +82° etc): used 251 g 98.7% NaOH + 1123 g 20.16% HCl theory 1114 (each case). The aq. dist. ~~acetone~~ took in all 220 cc N/10 NaOH (ph. ph. rate 6 drops; not over ½ cc C_2H_5OH added). Now distill off H_2O = 600 cc; & distill off 60 cc from this; and then from the 60 cc + 1st 5 cc sat. c. K_2CO_3 gave less than 0.3 cc C_2H_5OH (from ph ph) ∴ no CH_3OH can be present as had been proved before [see

The salts residues extr each 2× with 2 L Ether each time gave 49.7 g & 51.0 g gum sep. which combined & dissolved in 100 cc H_2O & extr 20× by ether gave 59.1 g C_3 lac gums $[\alpha]^{20}_D$ = +4.0 p = 4.0 acid got from H_2O solution 31.65 g C_5 gums A $[\alpha]^{20}_D$ = +24.0° p = 4.0 (this gum no ph. hydr 13 ...; with 5 cc ... 50 cc alc ∴ discarded) 5 cc of ... 1 L ether each got 16.45 g C_5 gums B $[\alpha]^{20}_D$ = +21.7 (p = 4.0)

Dee extr. salt residues in 4 lots 1× more with 1 L ether each got much C_5 gum C containing tar + Now ex to salt residues all with cold alcohol till snow white & got 14.8 g C_5 gums C with $[\alpha]^{20}_D$ NaCl ∴ ex to these again 5× R.T. with 1 L ether each time and got 34.0 g tar ∴ ex it R.T. with 250 cc ethyl acetate got 12.2 g C_5 gums D $[\alpha]^{20}_D$ = over +33° (p = 4.0) leaving ∴ 21.8 +28° and +30° could not get sharp reading p = 4.0). The residue now left weighed mood NaCl and tar (discarded).

Gums A	took up	88.5 g	Chinin & gave	31.87 g xx from alc	l. threo d. erythro Chinin m.pt 160–5	1st crops in all cases
Gum B	took up	43.0 g	Chinin & gave	18.45 g xx from alc	l. threo d. erythro Chinin m.pt 160–5	
Gum C	" "	40.0	" "	21.42 g	l. " " "	
" D	" "	32.0	" "	25.50 g	l. " " "	

∴ total l. threo d. erythro salt from A B C ~~+ D~~ = 97.24 g which with 45.0 g Baryt gave 67.32 g Chinin & 24.55 g l. threo d. erythro gum (alc extr); this treated with 73 g Brucin alc gave 110 g salts (1× sweep over) + on digesting this with 600 cc alcohol breaking up till all a granular powder which dissolved on cooling got ~~51.9~~ 53.9 g xx lle m.pt 170°–190° $[\alpha]^{20}_D$ = −27°.3 (p = 4.0) ∴ about 60% erythro + 40% threo salt. These xx from 20 cc H_2O + 250 cc alcohol, seeding with d. erythro salt m.pt 202°, gave rapidly in 24 hrs O.T. 21.21 g salts m.pt 190°–200° with $[\alpha]^{20}_D$ = −24°.9 (p = 4.0) and these rexx from 10 cc H_2O + 100 cc alcohol gave 16.35 g salts m.pt 198–200 $[\alpha]^{20}_D$ = −23°.2

which together with 4.96 g salt − 21°81 was used in oxid expt No 66 p 89
Have all rest of Brucin salts left in 3 fractions to work out acc. sep. of l. threo from (adding also 16.4 g Brucin salts from No 69 − p)
d. erythro in full + to get constants of each body accurately from ap. phenylhydrazides etc.
i.e. united as given + got 96.00 g salts which xx from 200 cc alcohol gave
45.85 g salts $[\alpha]_D^{20} = -27°6$ m pt 155°–160° ; the alc. filtr gave 37 g salts which xx from 22 cc thro
50 cc alcohol gave 13.23 g salts m pt 170°–175° ; unite these 58.08 g + xx from
+ 250 cc alcohol + got 22.9 g xxlle m pt 160° $[\alpha]_D^{20} = -29°24$ [Keep] → [hood Oct. 1, 10]
The alc. filtr cont. 35.18 g salts was dissolved in 80 cc alcohol this now in d.f. full of xxlle (Keep) hood Oct. 1
3rd portion is in a flask on shelf − about 22.0 g salts [Keep] → hood Oct 1

The orig alc. solutions obt. as filtrates from l. threo d. erythro Chinin xxlle from A B + C + D
still contained about 180 g Chinin salts since they gave no more xxlle from alcohol, now set free Oct 1–10
gum by 90 g $Ba(OH)_2$ + got 145.7 g Chinin + 44.9 g mobile gum (alc extr) → discard
This gum dissolved in 50 cc H_2O + extr 20 x by ether gave 17.0 g C_3 C_4 gums II $[\alpha]_D^{20} = +4°7$ (p = 4.0)
1 cc of this with 1 cc ph hyd + 1 cc alc gave only 0.1 g 1,3 Dioxy butyric ph hydr. ∴ discard all
and 24.5 g C_5 gums $[\alpha]_D^{20} = +22°3$ (p = 4.0) + these took up 62.0 g Chinin + gave 100 g salts (1 x sweep over cake) + on xx from 200 cc alcohol got 31.95 g corresp to l. threo d. erythro Chinin m pt 160–168°
with $[\alpha]_D^{20} = -113°1$ (p = 4.0) [Keep] ; alc. filtr gave no more ∴ set free gum by 25.0 g
$Ba(OH)_2$ etc + got 36.0 g Chinin and 14.85 g gum (alc extr) ; discard Oct 1–10
14.85 g gum in 15 cc H_2O + extr 20 X by ether was resolved into 5.75 g C_3 C_4 gums II $[\alpha]_D^{20} = +9°36$
∴ much C_5 gums (25% present) and into 8.4 g C_5 gums $[\alpha]_D^{20} = +19°83$ ∴ discard this as it
is obviously l. threo d. erythro gum mainly − On taking 1 cc of 5.75 g gum + 1 cc ph. hyd + 1 cc alc
got 0.7 36 hrs etc only 0.070 g 1,3 Dioxy butyric ph hydr m pt 125°–130° ∴ discard all

(71) Formose, 33% NaOH. March 1–10 – May 1 – 10 Feb 11 – 10
1/10 the size

Formose was made from 347 g c.a. 7. K's 35% CH_2O + 2984 g H_2O + 14.6 g $Pb(OH)_2$ boiling B.W.B. very hard
+ shaking frequently for 5 hrs + then add 7.65 g CrO_3 H_2 thro etc + got 17.5 g $PbCrO_4$ (theory 17.87 g) + got dist off
110 g crude Formose ; Now take a sol. of 275 g 98.54% NaOH in 450 cc H_2O (+38°) + shake + add the
formose diluted with 220 cc H_2O + rinse c 55 cc more H_2O (2 L flask as usual) + then heat B.W.B. then
(H_2O heap etc) ~~pour into~~ dilute with H_2O, + add 1230 g 20.22% HCl (theory 1221 g) + got (alc extr)
105 g gum ; on extr thus R.F. 3x with 1 L ether got 34.0 g very mobile gum ; since the portion left
insol in ether was very tarry 67 g ac. det it was acylated 7 hrs 100° with 210 cc anhydr + got 104 g acylated
gum of which 26.0 g tar + NaCl remained insol on extr with ether ; the acylated gums sol in ether,
70.85 g, were now lost by accident ∴ repeated, using 2 lots of 112 g + 113 g Formose + got
104.5 g gum A and 102 g gum B (alc extr) ; these acylated directly with 300 cc anhydr 7½ hrs 100° gave
gave 47.15 g + 44.80 g tar + NaCl mainly insol in ether. The ether sol. acylated gums were 101.65 g A and
103.0 g B : A gave on 1st hydr. with 3 pts H_2O 66.35 g gum A + B gave 66.6 g gum B
A " " 2nd " with 130 g $Ba(OH)_2$ + 300 cc H_2O 59.5 g gum A + B gave with 130 g $Ba(OH)_2$ + 300 cc H_2O 59.3 g gum
A + B were now each extr 3 X R.F. with 1.0 L ether each time + got
43.15 g soluble gum from A and 40.1 g sol. gums from B
got insol gum 18.33 g A and 21.15 g B

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On shaking A with 0.5 L cold ether got a resolution into 32.3 g sol gums and into {9.85 g insol gums
" " B " 0.5 L. " " " " " 31.5 g " " " " {8.60 g " "
Unite the cold ether extracts A+B 63.8 g (by diff) dissolve in 65 cc H_2O extr 5x and then 15x more
by ether 1st 5 extr took out 24.4 g C_3 C_4 gums I and 2nd 15 extr took out 17.65 g C_3 C_4 gums II
leaving (∴ by diff) 22.1 g gum in the H_2O solution; shook this in cold 2x with 250 cc ether
and got a resolution into 14.5 g soluble C_3 C_4 gums III and into 7.45 g insol gum which was
united with 9.85 g & 8.60 insol gums & ∴ total = 25.9 g these were then resolved by
dissolving in 2-3 pts ethyl acetate & cooling into 21.95 g soluble C_5 gums A and
into 3.9 g pptd gums B.
The 18.33 g gums A and 21.15 g gums B (see bottom p. 106) were now acylated with 530
64 cc anhydrid 7 hrs 100° & got 30.8 g acylated gums from A of which 6.48 g tar was insol.
and " 34.7 g " " " B, " " 8.73 g " " " water,
which on 1st hydr. c 3/4 H_2O gave 30.5 g gums &
The combined ethereal filtrates gave 49.35 g acylated gums
then with 60 g $Ba(OH)_2$ + 500 cc H_2O 8 hrs 100° got 27.4 g gum C.

The C_3 C_4 gums
The 24.4 g gums I made up to 1 L took 10 cc (∴ 0.244 g) took 24.84 $\frac{n}{10}$ NaOH ∴ treated gum with 15.0 g
→ corresp to 10.5 g dl lactic ∴
a total of 17.52 g (in 2 crops) air dry Zn dl lactate 3 H_2O
with 1 g $ZnCO_3$ etc.
Zn CO_3 etc (3.6 g insol) & got conc. aq. filtr etc etc. a total of 13.3 g (in 2 crops) air dry Zn dl lactate 3 H_2O
The 17.65 g gums II, made up to 1 L & took 15 cc (∴ 0.2647 g) took 27.41 cc $\frac{n}{10}$ NaOH ∴ treated gum with 1.0 cc phlyd
→ corresp to 8.05 g dl lactic ∴
(1.15 g insol) & got in conc. aq. filtr etc etc took 1.0 g of gum with $ZnCO_3$ etc but got no
The 14.5 g gum III, made up to 500 cc & take 10 cc (∴ 0.29 g) took 27.66 cc $\frac{n}{10}$ NaOH ∴
& ice etc v.t. seeding but got only 0.11 g m.p. 125-130° ∴ treated rest of gum 13 g + with $ZnCO_3$ etc & got ppt
xxlle of Zn lactate ∴ take all gum any zinc salts obtained from 3 gums I + II + III ppt
Zn by H_2S and got back 28.8 g C_3 C_4 gums (a) (ether extract) and 3.65 g gums A' (sol. in hot acetic ether).
(see p. 108)
The 21.95 g gum A was now dissolved in 44 cc H_2O & extr 20x by ether and got thus 9.08 g ~~C_3 C_4 gums IV~~ ether sol gums
which were shaken 2x in cold with 100 cc ether and got finally thus 7.05 g C_3 C_4 gums (b);
the insol part incl that left in H_2O were found to be 14.58 g gum A; tied also ~~3.65 g gum~~
~~A and~~ 3.9 g gum B and 27.4 g C. Now extract all these gums A, ~~B~~, B, C x R.T. with
ether and got as ~~foll~~ final result 19.8 g ether sol. gums; these dissolved in 20 cc H_2O &
extr 20 x by ether now gave 9.05 g more C_3 C_4 gums (c); there were left in H_2O sol 10.6 g A
stiff gums. The combined gums were extr R.T. by ether and evaporated to 25.85 g; these 3x.
dissolved, except 2.4 g tar, which was acylated etc gave back finally 1.18 g good gum), on digestion
with 500 cc ethyl acetate each time ∴ distill off solvent in W.B. to small volume and resolved gums into
16.0 g gum B easily sol. in cold acetic ether and into 9.51 g gum C not so soluble
It was at first thought no C_5 saccharins were present but large
amts are " ; furthermore

gums A B + C since they titrated mainly for C_6 saccharins were treated with Strychnine etc to get a resolution into the α dextro + galacto-metasacch. Strychnine salts which should come out from alcohol as xx salts – but got oils only ∴ n.g. ∴ set free gums again + got back [Ba(OH)₂ etc.] 10.05g A ; 14.45g gum B ; and 8.88g C.

A was now treated with 24.4g Brucin and gave by xx in all 10.48g Brucin salts crop I m.p. 180–188° + then 3.95g crop II m.p. 170°–180°

B was treated with 35.15g Brucin + gave by xx in all 5.3g Brucin salt m.p. 195°–202° had a total of
21.60 " + gave by xx " " 0.0g Brucin salts ∴ + 5.7g lost (see below)
(also 2.66g from 23.97g salts) also alc. filtr. from A, B + C united gum
C " incl. 4.24g (see below) [C_6 gums] m.p. 170°–202°. The alc. filtr. from A, B + C united gum
23.97g [treated] xx Brucin salts m.p. 170°–202°. The alc. filtr. from A, B + C united gum which extr. back with 40.0 gms $Ba(OH)_2$ etc got 61.2g Brucin and ? gms gum C_5 gums ; the extr residue
6x with 800cc ether (R.T.) dissolved 7.35g (2x) [fairly mobile] ; 5.79g (2x) [mobile] and 2.30g (2x) [little mobile] ; 4.6g viscous C_6 gums
1x with 800cc acetic ether got 6.47g C_6 gums and then with alc got [viscous] ∴ 7.0g C_6 gums } See p. 109
[viscous] ∴ 13.05g C_6 gums
(15.4g Brucin + gum back) 6.28g gum sol in acetic ether and 2.4g gum (alc extr.) which last two were united ∴

Gum C gave back 6.28g ... 9.05g (C) which ...
C_4 gums : Had 28.8g C_3, C_4 gums (a) and 7.05g (b) and 9.05g (C) which ... treated rest with 107g Brucin to give a total of 76.09g crude
16.1g gum : The 28.8g b.t. taking $\frac{1}{100}$ th titr. 27.50 cc $\frac{n}{10}$ NaOH ∴ treated rest with 107g Brucin ... and 10.65g
all in 3 crops (44.35g m.p. 194–203°; 24.25g m.p. 185–192°; 7.49g m.p. 180–187°) a total of 76.09g crude
+ crop x filtr from 16.1g gum with 45.0 Ba(OH)₂ etc 64.32g Brucin A' (p. 107)
1,3 Dioxy butyric Brucin ; the alc. filtrate gave + made with 3.65g gum A' ; on treating the 10.65g with 8g pure $ZnCO_3$
mobile gum (cold ether extr) and 5.55g stiff C_5 gum ; on treating the ... in dry xx zn dl lactate
alc got 2.88g mod $ZnCO_3$ + on conc aq. filtr adding alcohol alc got a total of 5.55g zinc salts only now discarded –
3 H_2O corresp to 3.36g dl lactic acid ; the aq. alc. filtrates, cont gummy zinc salts only now discarded –
The 16.1g gums taking $\frac{1}{50}$ th titr 29.06 cc $\frac{n}{10}$ NaOH (theory for C_4 lact = 3157cc) ∴ treat rest with 56.0g
Brucin etc and got in 3 crops (21.35g m.p. 194° ; 17.88g m.p. 185–190° ; 2.78g m.p. 180–5°) a total of 42.01g
1,3 Dioxy butyric Brucin ; the alc filtrates united (see above).
1,3 Dioxy butyric ph. hydrazide from the crude combined 13 Dioxy butyric Brucin 42.01g + 76.09g = 118.1g total
these gave with 45.0g $Ba(OH)_2$ etc 94.6g Brucin + 21.2g gum (ether extr) ; this mixed with 22cc ph.hydr. + 17.48g more 1,3 Dioxy butyric ph. hydrazide m.p. 128–132 (keep)
and 10cc alcohol gave 42 hrs O.T. seeding etc 17.48g more 1,3 Dioxy butyric ph. hydrazide ; used for rot. exptl. No (May 14–08 – 1.54g) + about 0.5g was
m.p. remained same on mixing with a prep from L. Ambrose. p = 4.0 α. E. D.
found ± abs. in a one dc tube
The 5.55g stiff gum + 3.65g gum A' ∴ total = 9.2g were now evap in open dish for 16 hrs with H_2O etc +
got back 7.15g gum ($\frac{1}{25}$ th titr. 23.75cc $\frac{n}{10}$ NaOH ∴ C_6 gums) ∴ treated with H_2O etc WB for 23 hrs longer +
got back 5.7g gum which with 17g Brucin extr 3x C_6H_6 etc gave 4.24g C_5 dl Brucin salt m.p.
195–210° ; the alc. filtrate now combined (see above) + worked up for free gum
C_5 metasaccharins The 23.97g Brucin salts obtained in 4 crops as stated above were now xx from 5cc H_2O + 100cc alcohol and got very rapidly 11.33g crop I [mp] which were enormously fairly thick but mobile
thought to be pure dl. erythro C_5 Brucin ; this gave with 5.0g $Ba(OH)_2$ etc 8.52g Brucin + 2.2g gum
(hot ether extr) + was resolved into 3/4 + 1/4 pts; 1/4 ∴ 0.5g with 0.5cc ph. hyd + 0.5cc alc gave
no xx hydrazide ∴ n.g. other 3/4 pt found 2 in 1dc tube (p = 4.0) was ± !! (keep)
The alc. filtrate from crop I now worked up for free gum uniting with other alc. filtrates as stated above

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C5 gums and C6 gums; summary   C5 gums: lost ether extracts (p 108)

(a) 7,35g; (b) 5.79g (c) 2,3g gum; besides 3/4 of 2.2g C5 dl erythro gum whose Brucin salt m.pt 200–210° – ? has it been treated with 4.7g Brucin?

C6 gums 13.05g gums, sol. in lost acetic ether – which were subsequently resolved into 5.90g gum easily sol. in sm. amt cold ethyl acetate and into 6,75g insoluble therein. and C6 gums (alc extr) containing 7.0g which were ∴ acylated with 21cc anhydride 8 hrs 100° gave 10.7g acylated gums of which 5,0g tar remained insoluble in ether. Hydrolysis of ether sol acylated gums by 15.0g Ba(OH)2 + 75cc H2O 7hrs 100 gave back 3.1g clean C6 gums

The C5 gums (a)(b)+(c) were all treated with Brucin on theory they were C5 lactones; aq. sol. extr 3× by C6H6 took out in all only 2,12g Brucin ∴ OK aq sol dist off in vacuo & xx from alcohol etc are giving various crops (20.63g ~~20.6~~ g in all) of dl erythro C5 + dl threo C5 salts which are on hand under hood.

The C6 gums (in 3 parts): of the the 5.9g gum + the 6.75g gums were treated with Brucin extr 3× C6H6 etc but up to date had got no xx of Brucin salts after removing H2O in vacuo & xx from alcohol – under hood all summer) – Same Σ – 3.1g on hand gave no xxlle

(72) Mixture of d threo C5 Chinin with eq. amt mixture of l threo d. erythro Chinine

Took 2,0g d. threo C5 Chinin m.pt 174° (May 14, 09) and 2,0g l. threo d erythro C5 Chinin m.pt 165° (May 12–09) + dissolved these in 30cc alcohol: on cooling got a separation of 2.2g xx needles m.pt 170° and this re-xx once more from 20cc alcol. alcohol gave 1,24g (?) d. threo C5 Chinin m.pt 174° with $[\alpha]_D^{20} = -105°.2$ (p = 4.0); the alc. filtr from crop I distilled off in vacuo 60° & dissolved salt (1.8g by diff) in 5cc alcohol now gave rapidly 0,35g xx needles m.pt 160°–165° – this indicates that a mixture of all 4 C5 metasaccharins ought to be partially separated through xx of their Chinin salts.

(73) Formose + Ca(OH)2: Feb 17–10 April 1–10   Nov 24–08 → cf No 44 – continuation

Took the 96.0g Formose + Ca(OH)2 gum (Sept 15–08) ~~of 40~~ when the Ba(OH)2 had not been removed by Oxalic acid as was subseq. done before ~~evap~~ dist off the Formose from aq. sol at reduced pressure

acylated with 300 cc anhydr 7 hrs 100° & got 160g acylated gums of which 50.4g remained insol in ether & got from ether sol. acylated gums on 1st hydr 62.7g gums – or after 2nd hydr. with 150g Ba(OH)2 etc got 58.7g Saccharins distributed as follows.

30,55g A (5 × 1 L.R.7.
17,65g B (acetic ether extr)
10,50 C (alc extr)

B + C were quite tarry ∴ had to acylate again & got only 1.6g tar from B and 4.3g tar from C & got back from B + C combined 20,5g gums (hydr. c. Ba(OH)2 and)

Had also follow. amts. of Saccharin gum from ether Formose expt. (NO 44)

6.8 g gum from 180–200° m.pt. Brucin salts; 8.5 g gum A: 16.4 g B ∴ total = 31.7 g

also have 7.35 g gum C — or 4.78 g C after a 2nd acetylation. See Nov 24 –08

The 31.7 g Formose gums were now united with the 30.53 g hydr. c Ba(OH)₂ gums A (see p. 109) & the gums

dissolved in 100 cc H_2O + xx + 20 x by ether gave 19.05 g ~~C3 C4 gums~~ ether sol. gums & these

Shaken in cold with 200 cc ether all dissolved except 1.65 g gum ∴ put with aq. sol.)

The cold ether extr contained acc. det ∴ 17.4 g C_3 C_4 gums.

The aq. sol. gave back 39.25 g gums which were now united with the 20.5 g gums (p 109)

& these then extr 5 X R.T. with 500 cc Ether each time when got a dissolution into

20.8 g soluble and fairly mobile C_5 gums and into ~~gum~~ above, is now all clean Sacch gums.

38.0 g insol. gums which, with 4.78 g gum C ~~gum~~ above, is now all clean Sacch gums.

The 38.0 g gums were now dissolved by digestion R.T. 100 cc ethyl acetate cool etc into

$\frac{1}{50}$ th took 21.23 cc $\frac{n}{10}$ NaOH

16.45 g easily soluble gums and into other 19.7 g insol. gums which united with the 4.78 g C gum

above makes a total of 24.15 g (acc det) C_6 gums.

→ The 20.8 g gum was now extr 4 X R.T. by 400 cc ether each time and all but 4.45 g which was

united with 16.45 g lot dissolved. By acc. det 16.3 g C_5 gums dissolved in the last ether:

$\frac{1}{50}$ th of the 16.3 g gum took 25.11 cc $\frac{n}{10}$ NaOH (theory for C_5 lactone = 24.70 cc) ∴ this gum 16.0 g

was treated with 48.0 g Brucin & xx by xx from alc 20.4 g, crop I, m.pt 188–198°; dl erythro C_5 Brucin

probably since on xx from 7 cc H_2O + 100 cc alcohol got 10.45 g salts m.pt 200–208° 4 sided prisms

got then 13.45 g crop II salts m.pt 180–183° & then no more.

The C_3 C_4 gums, 17.4 g, on taking $\frac{15}{100}$ ths (∴ 0.261 g) required 24.56 cc $\frac{n}{10}$ NaOH ∴ treat rest of aq. sol

with 63.0 g Brucin & xx by xx alc 12.78 g m.pt 185–198° crop I; 11.78 g, crop II, m.pt 185–190° crude 1,3 Dioxy butyric

Brucin & then no more; the combined salts ∴ 24.56 g gave with 10 g Ba(OH)₂ etc 18.18 g Brucin and

4.45 g gum (ether extr): on mixing this with 4.5 cc ph. hydr + 2.5 cc alc got seeding R.T. 42 hrs 1.45 g 1,3 Dioxy

butyric ph. hydrazide m.pt 128–132°; proved by 0.5 g was ± optically in 4.0% conc & also

found m.pt same on mixing with a similar prep from l. Arabinose May 14 – 08

The alc. filtr from the 2 crops Brucin salts had 58.0 g salts which with 30.0 g Ba(OH)₂ etc

gave 41.88 g Brucin & 5.83 g mobile oil (cold ether extr) & then 0.95 g still stiff gum (hot ether extr) in which

then 3.5 g (alc extr) ∴ were lost 2 gums = 4.45 g. The 5.83 g (cold ether extr) on titration

taking 0.2332 g took 22.34 cc $\frac{n}{10}$ NaOH ∴ treated rest of aq. sol with 4.0 g $ZnCO_3$ etc (1.35 g insol $ZnCO_3$)

+ got a total of 2.6 g Zn dl lactate xx 3 H_2O [corresp to 1.56 g dl lactic acid, Q.E.D.]

It is evident that a very large amt of these are present and that only the 4 (15 g)

C_5 gums Cometasaccharins are there. Tried to get from the dl. erythro C_5 Brucin salts melting above 200° by Ba(OH)₂ & then by Chinin a resol. into d. erythro C_5 Chinin in which is very diff sol. in alcohol & into l. erythro C_5 Chinin which must be easily soluble but did not succeed

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~~prob~~ probably because the salt had 1 3 oxy butyric acid as well as d l threo C_5 gum also present ∴ must repeat in fall; for same reason an expt with ph. hydr & alcohol & 0.5 gm failed also because C_4 & C_5 Isosaccharins are present (cf. experiments 19~~10~~-12)