is used in naming ring compounds having the sulfur in the ring, it is not the name of a substituent but a part of the index name; as, Thiopyran, methyl- (not Pyran, methylthio-).

Columbus, Ohio.

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

THE METHOD OF OXIDATION AND THE OXIDATION PRODUCTS OF *l*-ARABINOSE AND OF *l*-XYLOSE IN ALKALINE SOLUTIONS WITH AIR AND WITH CUPRIC HYDROXIDE.[1]

By J. U. Nef, Oscar F. Hedenburg and J. W. E. Glattfeld.

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Nef published his first work on the oxidation of sugars by Fehling's solution, or, more correctly, by a suspension of cupric hydroxide in an alkaline sugar solution, in Liebig's *Annalen* in 1907.[2] The sugars studied were *l*-arabinose, *d*-glucose, *d*-mannose and *d*-fructose. Thereafter a series of investigations was undertaken by Nef, in part in collaboration with his students.[3]

The present work was undertaken in order to obtain more complete information with regard to the amounts of the oxidation products. Experimental proof of the production of certain acids, such as ribonic acid, was sought for.

When *l*-arabinose was oxidized in alkaline solutions by air, *l*-erythronic, *d*-threonic, *d*- and *l*-glyceric, glycollic, formic and carbonic acids were produced. When oxidation was accomplished by cupric hydroxide, *l*-arabonic, *l*-glyceric, glycollic, oxalic, formic and carbonic acids were found among the oxidation products. *l*-Ribonic acid was not found, although it was presumably produced, for *d*-lyxonic acid was found among the oxidation products of *l*-xylose. Other products of oxidation of *l*-arabinose were obtained by Nef in former experiments.[4]

When *l*-xylose was oxidized in alkaline solutions by air, *l*-threonic, *d*-erythronic, *l*-glyceric, glycollic, formic and carbonic acids were found to be present among the products. When oxidation was accomplished

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[1] The experimental work described in this paper was done by Dr. Nef during the two years previous to his death on August 13, 1915, with the assistance of Dr. Glattfeld and myself. I have undertaken to prepare the results of the work of this period for publication. Dr. Glattfeld has assisted in the preparation of this paper.—Oscar F. Hedenburg.

[2] *Ann.*, **357**, 214 (1907).

[3] Anderson, *Am. Chem. J.*, **42**, 401 (1909); Spoehr, *Ibid.*, **43**, 327 (1910); Glattfeld, *Ibid.*, **50**, 137 (1913); Nef, *Ann.*, **403**, 282 (1913); C. C. Todd, dissertation published by the University of Chicago Press.

[4] *Ann.*, **357**, 251 (1907).

by cupric hydroxide, *l*-xylonic, *d*-lyxonic, glycollic and oxalic acids were proved to be present among the products.

Nef discussed the theory of the oxidation of *l*-arabinose by Fehling's solution in Liebig's *Annalen* in 1907.[1] A thesis[2] produced by one of us under Nef's direction gives a theoretical discussion of the oxidation of *d*-glucose in alkaline solutions by air and by hydrogen peroxide, and the same theory may be applied to the oxidation of any sugar in alkaline solutions.

Experimental Part.

***l*-Arabinose and Air.**—An aqueous solution of 50 g. of *l*-arabinose was added rapidly to a solution of 109.2 g. of 85.5 per cent. potassium hydroxide (5 equivalents) in 5000 cc. of water, which made the water content of the flask 5500 cc. Air,[3] freed from carbon dioxide, was at once drawn through the solution at 20°. The temperature of the solution was raised rapidly to 38–41°. The sugar was oxidized completely in 22 hours. At the end the solution was colorless and strongly alkaline. One per cent. more than the theoretical amount of hydrochloric acid necessary to convert all the potassium hydroxide used into the chloride was then added and the solution was distilled *in vacuo* nearly to dryness. The residue was freed from traces of formic acid by being dissolved twice in small amounts of water with subsequent distillation *in vacuo*.

Carbon dioxide was not determined.

Formic Acid.—The amount of this acid was determined by titration of an aliquot part of the aqueous distillate, which contained no hydrochloric acid. There were found 15.35 g. of formic acid. Therefore, 20.03% of the total carbon of the sugar was oxidized to formic acid.

Non-Volatile Acids.—The non-volatile acids, separated from potassium chloride by extraction with absolute alcohol, weighed 41.2 g. with $[\alpha]_D^{20} = +26.46°$. These acids were resolved into 24 g. of a gum called "A," soluble in 500 cc. of boiling ethyl acetate, 10.25 g. of a gum called "B," soluble in a second portion of 500 cc. of boiling ethyl acetate, and 5.5 g. of a residue containing potassium salts. The residue yielded 2.4 g.[4] of a gum called "C."

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[1] *Ann.*, **357**, 252 (1907).

[2] *Am. Chem. J.*, **50**, 135 (1913).

[3] The air entered the solution through four bent tubes, the ends of which were 90° apart; each tube terminated in a flattened bulb, 2.25 cm. in diameter, and from each bulb radiated six symmetrically arranged capillary tubes, 1 cm. long.

[4] The residue was dissolved in 15 cc. of 5.6 normal hydrochloric acid and the solution was distilled *in vacuo*. The resulting gum was freed from potassium chloride by solution in absolute alcohol. The alcoholic solution yielded on distillation *in vacuo* 3.36 g. of gum (+28.28°) from which 2.36 g. were extracted by boiling ethyl acetate. The residue was heated with acetic anhydride, the excess of which was removed by distillation *in vacuo*. The acetylated gum was extracted with ether and the ether-soluble gum was saponified with barium hydroxide. After removing the barium from the solution, it was distilled *in vacuo* and yielded 0.4 g. of gum which was united with the 2.36 g. lot.

Gum "A," 24 g., was resolved further by two extractions with cold ether into 10.87 g. (+14.26°)[1] of soluble gum and 13.13 g.[2] of a partly crystalline residue called gum "D." The aqueous solution of the soluble gum was treated with 50 g. of 92% brucine.[3] Two crops of brucine salts, 13.76 g. all in all, melting between 204° and 206° and with $[\alpha]_D^{20} = -28.4°$, were obtained from alcoholic solution and united with similar salt (see below).

Glycollic Acid.—The uncrystallizable residue of brucine salts, left after the separation of 13.76 g. of crystallized salt, was decomposed in aqueous solution by 19 g. of crystallized barium hydroxide and yielded 31.21 g.[4] of brucine and 7.7 g. of a mobile gum. This gum was resolved by boiling ether (500 cc.) into 2.7 g.[5] of an insoluble gum and 5 g. of crude, ether-soluble glycollic acid gum (+4°). The hot, aqueous solution of the latter dissolved 17.86 g. of strychnine. After distillation *in vacuo*, the crude strychnine salts were dissolved in aqueous alcohol, and 17.18 g.[6] of strychnine glycollate (two crops), melting from 140–200°, were obtained. This salt, on decomposition with barium hydroxide, yielded 14.43 g. of strychnine and a solution of glycollic acid. This solution dissolved 1.96 g. of calcium carbonate and then yielded on concentration a total of 3.73 g. of calcium glycollate, $Ca(C_2H_3O_3)_2.4H_2O$, which was equivalent to 2.71 g. of glycollic acid. 1.9545 g. of salt lost 0.5291 g. of water at 100–105°.

Calculated for $Ca(C_2H_3O_3)_2.4H_2O$: H_2O, 27.48. Found: 27.08. 0.4286 g. of anhydrous salt gave 0.1265 g. of CaO. Calculated for $Ca(C_2H_3O_3)_2$: CaO, 29.47. Found: 29.52.

***l*-Erythronic γ-Lactone.**—Gum "D," 13.13 g.,[7] dissolved in hot ethyl acetate. After concentration this solution yielded 4.57 g. of *l*-erythronic γ-lactone, Crop I, melting at 102–103° and with $[\alpha]_D^{20} = +72.53°$, *i. e.*, 0.5562 g. of lactone dissolved in 14.1128 g. of water gave $\alpha = +2.78$ in a 10 cm. tube; $d = 1.011$. According to Ruff,[8] the melting point of this

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[1] The specific rotation will be given usually in brackets. It was determined in 4% solution, or as near that value as possible.

[2] This material was proved later to contain *l*-erythronic lactone.

[3] After the solution had become alkaline because of the formation of brucine salts and the solution of an excess of brucine, it was heated one hour on a boiling water bath. After cooling, the solution was extracted five times with benzol to remove the excess of alkaloid and distilled *in vacuo*.

[4] After filtering off the crystalline brucine, the alkaline solution was extracted five times with benzol to remove traces of brucine. The barium was removed by sulfuric acid. The solution was adjusted so as to contain a trace of barium, and distilled *in vacuo*.

[5] Of this gum 1.2 g. dissolved in boiling ethyl acetate (lost by accident) leaving 1.5 g. of tarry gum.

[6] The uncrystallizable strychnine salts, 6.1 g., yielded on decomposition with barium hydroxide 2.47 g. of strychnine and a gum which was used later.

[7] See above.

[8] *Ber.*, **34**, 1369 (1901).

lactone is 109° (cor.) and $[\alpha]_D^{20} = +71.74°$. Gum "B," 10.25 g., also dissolved in ethyl acetate, yielded 3.06 g. of this lactone melting at 96–98°, and with $[\alpha]_D^{20} = +71.75°$. The ethyl acetate filtrates were combined and concentrated, whereupon 3.17 g. more of the lactone, melting at 98–101°, and with $[\alpha]_D^{20} = +69.3°$, separated out.

By titration, 0.2801 g. of lactone from Crop I required 23.75 cc. of 0.1 *N* KOH for neutralization, which was exactly the theoretical for $C_4H_6O_4$.

***l*-Erythronic Phenylhydrazide.**—The aqueous solutions used in observing the optical activity above were combined and on distillation *in vacuo* yielded 1.6 g. of gum, which gave on treatment with 2 cc. of phenylhydrazine and 4 cc. of absolute alcohol a solid mass of crystals. Pure *l*-erythronic phenylhydrazide, 2.64 g., melting at 126–127° and with $[\alpha]_D^{20} = -17.29°$, was obtained.

The ethyl acetate filtrate from 3.17 g. of lactone (see above) yielded no more crystals and the gum recovered on distillation was united with gum "C," 2.4 g.[1] The combined gums, 12.7 g. (+30.31°), were treated in hot, aqueous solution with 52 g. of 92% brucine in the usual way. After distillation in a vacuum, 72.75 g. of brucine salts, still containing water, were obtained and yielded on crystallization from aqueous alcohol three crops of crystalline salts, in all 39.79 g., melting at 205–7° and with $[\alpha]_D^{20} = -29.67°$ to $-30.28°$. The gummy brucine salts from the mother liquor, 21.8 g., gave back on decomposition with barium hydroxide 12.12 g. of brucine and 4.05 g. of gum (+6°) of which 2.65 g. dissolved in ethyl acetate (lost by accident), leaving 1.4 g. of tarry gum. This gum was united with 1.5 g.[2] of tarry gum and together they were acetylated with acetic anhydride. After the excess of anhydride had been distilled off *in vacuo* the acetylated gum was extracted with ether. The ether-soluble gum was recovered and saponified with barium hydroxide. After removing barium the solution was distilled *in vacuo*. The gum was united with that from 6.1 g. of gummy strychnine salts (footnote, page 1640) giving 2.05 g. of gum (+3.66°). The brucine salts prepared from this material yielded on crystallization from alcohol 2.45 g. of salts[3] melting from 190–200°.

There have been obtained thus far 56 g. of high-melting brucine salts[4] which were decomposed in aqueous solution with 26 g. of crystalline barium hydroxide; 43.28 g. of brucine and 12.3 g. of gum (+35.15°) were recovered. No *d*-threonic phenylhydrazide was obtained by

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[1] Cf. page 1639.

[2] Cf. footnote, page 1640.

[3] The alcoholic filtrate gave back 6.6 g. of gummy brucine salts. These yielded, on decomposition with barium hydroxide, a gum which was shown later to contain glyceric acids.

[4] These include 13.76 g. (page 1640), 39.79 g. and 2.45 g. (see above).

treating 0.8 g. of this gum with phenylhydrazine. The rest of the gum, 11.5 g., gave two crops of *l*-erythronic γ-lactone, 2.15 g. (+71.7°) and 0.47 g., melting between 95° and 102°. The remaining gummy acids, 8.7 g., were resolved into 3.25 g. (+19.69°) soluble in ether and 5.06 g. (+28.28°) soluble in ethyl acetate. From the latter 0.42 g. of *l*-erythronic lactone was obtained, leaving 4.59 g. of gum (+23.52°).

***d*-Threonic Phenylhydrazide.**—*d*-Threonic γ-lactone has not been obtained crystalline. Its most characteristic derivative, the phenylhydrazide, is easily obtained when only small amounts of other phenylhydrazides are present. It melts at 157° and possesses $[\alpha]_D^{20}$ = about +29°.

The aqueous solutions of the above gums, 4.59 g. and 3.25 g., were treated in the usual way with brucine. The crude salts yielded, on crystallization from alcohol, in the first case, 14.48 g.[1] of salts melting from 203–208° with $[\alpha]_D^{20}$ = —27.57° to —29.22°; and in the other, 11.44 g.[1] of salts melting from 200–210° with $[\alpha]_D^{20}$ = —26.72° to —27.87°. Both lots of salts were combined and digested with a mixture of 5 cc. of water and 250 cc. of absolute alcohol for one hour under a reflux condenser, whereupon 17.9 g. of crystalline plates remained insoluble.[2] On decomposition with barium hydroxide these crystals gave back 13.92 g. of brucine and 4.52 g. of gum (+28.7°). On treatment with phenylhydrazine this gum yielded no *d*-threonic phenylhydrazide because of the presence of other phenylhydrazides. The gum was recovered by decomposition of the gummy phenylhydrazides with barium hydroxide and weighed now 3.7 g. It was converted again into brucine salts in the usual way. The crude salts, 17.96 g., on crystallization from aqueous alcohol yielded 5.85 g. of salts melting at 209° with $[\alpha]_D^{20}$ = —28.08°. The brucine salts recovered from the filtrate were digested with boiling absolute alcohol and 5.62 g. of salts melting at 210–212° remained insoluble; these were united with 4.98 g.[3] of brucine salts melting at 205° and together recrystallized from aqueous alcohol. There separated out 5.31 g.[4] of brucine salts melting at 208° with $[\alpha]_D^{20}$ = —28° which were united with the 5.85 g. lot above. The combined salts, on decomposition with barium hydroxide, gave back 8.5 g. of brucine and 2.48 g. of gum (+35.1°) which from solution in ethyl acetate yielded 0.25 g. of *l*-erythronic γ-lactone melting at 100–103°. The filtrate gave back 1.96 g. of gum which on treatment with 2 cc. of phenylhydrazine and 2 cc. of absolute alcohol

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[1] The gummy brucine salts recovered from the mother liquors weighed 4 g. and 4.45 g., respectively, and were used later.

[2] The alcoholic filtrate gave back 8.62 g. of salts which on decomposition with barium hydroxide yielded 5.14 g. of brucine and 1.75 g. of crude glyceric acid gum (+4.53).

[3] Cf. page 1643.

[4] The alcoholic filtrate gave back 4.9 g. of salts.

yielded 0.68 g. of phenylhydrazide melting between 150° and 156° with $[\alpha]_D^{20} = +28.34°$. By recrystallization from 20 cc. of absolute alcohol 0.45 g. of pure *d*-threonic phenylhydrazide melting at 157° was obtained.

0.2157 g. of substance gave 0.1224 g. H_2O and 0.4182 g. CO_2.

Calc. for $C_{10}H_{14}O_4N_2$: C, 53.10; H, 6.19. Found: C, 52.89; H, 6.31.

d- **and** *l*-**Glyceric Acids.**—These acids were obtained from several lots of gummy brucine salts. Three lots,[1] 6.6 g., 4 g., and 4.45 g., united and decomposed by barium hydroxide, gave back 3.15 g. of stiff gum of which 1.06 g. (+2.35°) dissolved in boiling ether. The residue was heated with acetic anhydride. The acetylated gum, freed from excess of anhydride by distillation *in vacuo*, was extracted with ether. The ether-soluble gum, on saponification with barium hydroxide, yielded 0.5 g. of gum (+20°) which was united with 1.06 g. and 1.75 g.[2] lots of gum. The combined gums weighing 3.1 g. were converted into brucine salts. After distillation in *vacuo* 17.05 g. of crude brucine salts were obtained which gave by crystallization from aqueous alcohol[3] 4.98 g.[4] of salts melting at 205°. The residual brucine salts, 12.25 g., yielded, on crystallization from absolute alcohol, 4.09 g. of salts melting at 205°. These salts, united with 4.9 g. of brucine salts (footnote, page 1642) and together recrystallized from absolute alcohol, yielded 7.7 g.[5] of brucine *d*,*l*-glycerate. On decomposition with barium hydroxide these salts gave back 5.18 g. of brucine and 1.55 g. of gum (+3.87°) the aqueous solution of which dissolved 4.75 g. of quinine.[6] From the solution of these salts (5.88 g.) in 12 cc. of water 0.33 g. of quinine *l*-glycerate melting at 165–7° separated out. This salt crystallizes out of much water whereas quinine *d*-glycerate does not. On distillation under diminished pressure 5.45 g. of salts were recovered from the mother liquor; from a solution of these in 10 cc. of absolute alcohol 1.66 g. of quinine *d*-glycerate melting at 182° and with $[\alpha]_D^{20} = -124°$ were obtained. This salt gave back, on decomposition with barium hydroxide, 1.17 g. of air-dried quinine and 0.4 g. of gum (+5.69°), the aqueous solution of which dissolved 0.22 g. of

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[1] Cf. footnotes, pages 1641 and 1642.

[2] Cf. footnote page 1642.

[3] Brucine salts were usually dissolved in two volumes of alcohol; *i. e.*, 17 g. of salts were dissolved in 34 cc. of absolute alcohol by heating. On cooling some gummy salts usually separated out and were brought into solution by adding small amounts of water until the solution was homogeneous.

[4] Cf. page 1642.

[5] The alcoholic mother liquor was united with that from the 4.09 g. lot of brucine salts above. The gummy brucine salts (8.32 g.) recovered by distillation *in vacuo* were decomposed by barium hydroxide. The recovered gum, 1.6 g., lost 0.5 g. of glycollic acid by evaporation of the aqueous solution on a boiling water bath (cf. *Ann.*, 403, 255 (1913)). The residue yielded no quinine *d*- or *l*-glycerate.

[6] Traces of free quinine were removed from the cooled solution by five-fold extraction with ether.

calcium carbonate. The gummy calcium *d*-glycerate (0.44 g.) was precipitated from solution in an equal weight of water by alcohol in a porcelain dish and rubbed with a pestle until it became crystalline. It melted at 138° and possessed $[\alpha]_D^{20} = -9.66°$. The pure salt[1] gives $[\alpha]_D^{20} = -14°$.

***l*-Arabinose and Cupric Hydroxide.**—A suspension of cupric hydroxide in an alkaline solution was prepared by treating a solution of 382.5 g. of crystallized copper sulfate in 2000 cc. of water with 301 g. of 85.5 per cent. potassium hydroxide dissolved in 688 cc. of water. Fifty grams of *l*-arabinose, dissolved in 100 cc. of water, were now quickly added with 150 cc. of rinsings to the alkaline solution which was shaken thoroughly at the same time. The temperature of the mixture was kept at 60–70° for a short time and then raised rapidly to the boiling point of water, where it was maintained for one hour. Two portions of the sugar of 50 g. each were oxidized. The solutions were combined after the cuprous oxide had been removed by filtration. The combined filtrates were cooled and 112.3 g. of concentrated hydrochloric acid (sp. gr. 1.19) added. Copper, present in traces in the solution, was removed by hydrogen sulfide. After distillation *in vacuo* nearly to dryness the organic acids were separated from salts by solution in alcohol. The mixture of potassium sulfate and chloride weighed 759.5 g., whereas the theoretical amount would have been 762.4 g.

The alcoholic solution yielded, on distillation under diminished pressure, a mobile gum weighing 97 g. containing some hydrogen chloride. Three liters of ether extracted 34.6 g. of which 33 g., called gum "A," remained in solution after concentration to 2000 cc. and 1.6 g. (—14.66°) separated out. The part insoluble in 3 liters of ether was dissolved in absolute alcohol. This solution was filtered and distilled *in vacuo*. The recovered gum, 39 g. (—16.66°), was united with the 1.66 g. lot. From the combined gums boiling ethyl acetate (500 cc.) extracted 20.2 g. of gum (—13.12°) of which 9.05 g. (—5.96°), called gum "B," were dissolved in boiling ether (1000 cc.) leaving 10.7 g. of gum (—20°). The gum insoluble in ethyl acetate, 19.5 g., was treated in aqueous solution with 2 cc. of concentrated hydrochloric acid to decompose potassium salts. From the gum, recovered by distillation *in vacuo*, 10.76 g. (—23.95°) were extracted by ethyl acetate and then from the residue 3.9 g. of gum (—22.56°) were extracted by acetone. The aqueous solutions of the gums, 10.7 g., 10.75 g. and 3.9 g., were combined and after distillation *in vacuo* 25.35 g. of gum, called gum "C," were recovered.

Oxalic and Glycollic Acids.—The aqueous solution of gum "A," 33 g., dissolved 66.05 g. of strychnine. On concentration of the aqueous solution of salts 8.1 g. of secondary strychnine oxalate melting from 265–270°

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[1] *Am. Chem. J.*, **42**, 423 (1909).

separated out. The aqueous filtrate was distilled *in vacuo* and the gummy strychnine salts recovered were dissolved in two parts of 95 per cent. alcohol by heating. On cooling 18.46 g. of strychnine salts crystallized out, which by recrystallization from water gave 1.45 g. of secondary strychnine oxalate, leaving 17.01 g. of crude strychnine glycollate.[1] The salts recovered from the alcoholic mother liquor by distillation *in vacuo* yielded from solution in two parts of alcohol 15.58 g. of strychnine glycollate.

The aqueous solution of gum "B," 9.05 g., dissolved 18.68 g. of strychnine. The crude salts, obtained by distillation *in vacuo*, yielded from alcoholic solution 7.31 g. of strychnine glycollate[1] melting from 150–195° with $[\alpha]_D^{20}$ = —24.56°.

The 17.01 g. lot of salt yielded, on decomposition with barium hydroxide, 2.95 g. of gum (—4.07°), and the 15.58 g. and 7.31 g. lots of salt combined gave 4.35 g. of gum (—2.53°). The aqueous solution of the united gums was evaporated on a boiling water bath for several hours, whereby glycollic acid was volatilized, and the residual gum weighed 4.38 g. (—7.53°). Therefore, 2.92 g. of glycollic acid were expelled by this treatment.[2]

The two crops of secondary strychnine oxalate, combined (9.56 g.) and decomposed by 41 cc. of *N* KOH, yielded 7.84 g. of strychnine. The alkaline solution was treated with 43 cc. of *N* HCl. After distillation *in vacuo* the residue was extracted with ether and 1.38 g. of oxalic acid were recovered from the ethereal solution.

***l*-Arabonic γ-Lactone.**—The aqueous solution of gum "C," 25.35 g., dissolved 46.34 g. of strychnine and after distillation *in vacuo* 86 g. of partly crystalline salts were obtained. From the solution of these in 150 cc. of absolute alcohol 19.18 g.[3] of crude strychnine *l*-arabonate, melting between 160° and 170° with $[\alpha]_D^{20}$ = —19.78°, separated out. On decomposition with barium hydroxide this salt yielded 11.75 g. of strychnine and 5.8 g. of gum (—41.4°). From solution first in acetone and then in ethyl acetate, this gum yielded in several crops 3.21 g. of crude *l*-arabonic γ-lactone melting between 92° and 98° with $[\alpha]_D^{20}$ = —66.66°. On recrystallization from acetone 2.63 g. of this yielded 1.15 g. of lactone melting at 96–8° with $[\alpha]_D^{20}$ = —69.2°.

Unidentified Material.—There were several lots of gum,[4] 13 g., 8.9 g.,

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[1] The uncrystallizable strychnine salts were united and weighed 72.26 g. On decomposition with barium hydroxide there were obtained 46.42 g. of strychnine and 23.26 g. of gum, of which 13 g. (—1°) dissolved in ether and 8.9 g. (—7.9°) dissolved in ethyl acetate. The residue, 2.25 g., was discarded.

[2] *Ann.*, 403, 255 (1913).

[3] The mother liquors gave back uncrystallizable salts which, on decomposition with barium hydroxide, yielded 17.6 g. of gum (—10.4°).

[4] See above; also page 1646.

4.38 g.[1] and 17.6 g.,[1] which were not resolved into constituents. Brucine salts were first prepared from them, but crops of crystalline salts obtained were not homogeneous, and could not be separated by recrystallization into components. The gums were recovered and attempts were made to obtain re-solution by means of basic lead acetate solutions. On adding aqueous solutions of the gums to basic lead acetate solutions insoluble lead salts were precipitated. The soluble and precipitated lead salts were decomposed by hydrogen sulfide, but the recovered gums were proved by observation of the optical activity to be similar.

l-Xylose and Air.

Fifty grams of *l*-xylose were oxidized by air in an alkaline solution in the same way as *l*-arabinose.

Formic Acid.—The aqueous distillate contained 13.17 g. of formic acid (no hydrochloric acid being present). Therefore 17.16% of the total carbon of the sugar was oxidized to formic acid.

Non-Volatile Acids.—The acid gum, 43.1 g. (—7.87°), was separated from 124.41 g. of potassium chloride by solution in absolute alcohol. The gum, extracted with four portions of boiling ethyl acetate (250 cc. each), lost (by difference) 36.9 g. The residue, 6.2 g., was dissolved in a few cc. of hydrochloric acid and distilled *in vacuo*. After acetylation with acetic anhydride the excess of anhydride was distilled off *in vacuo*. The ether-soluble portion of the acetylated gum yielded on saponification 4.1 g. of gum. The aqueous solution of this gum was united with that of 36.9 g. of gum and after distillation *in vacuo* 38.3 g. of gum were recovered. From this 17.8 g. of gum (—13.9°), called gum "A," were extracted with boiling ether (50 cc.), leaving 20.5 g. (—13.66°) called gum "B."

Derivatives of *l*-Threonic Acid.

The aqueous solution of gum "A," 17.8 g., was treated with 75 g. of 92% brucine. After distillation *in vacuo* the recovered brucine salts were dissolved in alcohol. Two crops of crystalline brucine salts, 27.25 g. (m. p. 208°, $[\alpha]_D^{20}$ = —30.55°) and 12.05 g. (m. p. 205°, $[\alpha]_D^{20}$ = —29.3°), were obtained. The aqueous solution of gum "B," 20.5 g., was treated with 80 g. of brucine. After distillation *in vacuo* the recovered brucine salts yielded from alcoholic solution three crops of salts, 41.15 g. (m. p. 208°, $[\alpha]_D^{20}$ = —31), 17.77 g. (m. p. 206°, $[\alpha]_D^{20}$ = —29.93°) and 7.83 g. (m. p. 203°, $[\alpha]_D^{20}$ = —28.8°). The five crops of high-melting brucine salts[2] were united with two other crops, 2.63[2] g. and 5.4 g. (melting at

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[1] See above; also page 1645.

[2] The gummy brucine salts, 50 g. from gum "A" and 36 g. from gum "B," recovered from the alcoholic mother liquors, yielded on decomposition with barium hydroxide 10.41 g. of gum (—2.69°) and 6.75 g. of gum (+4.15°), respectively. From the former boiling ether dissolved 4.41 g. of gum (—5.44°) and then ethyl acetate dissolved from the remainder, 6 g., 2.1 g., leaving 3.9 g. of tarry gum. From the 6.75 g. lot of gum ethyl acetate dissolved 4.95 g. of gum leaving 1.8 g. of tarry gum. The

195° to 200°), making a total of 114.08 g. of salts. After decomposition in aqueous solution with 52 g. of crystallized barium hydroxide, these salts yielded 87.4 g. of brucine and 24.9 g. of gum (—18.84°). On treatment with 26 cc. of phenylhydrazine and 33 cc. of absolute alcohol this gum yielded 15.18 g. of crude *l*-threonic phenylhydrazide melting at 157–8° with $[\alpha]_D^{20} = -30.45°$. From the alcoholic filtrate 30.5 g. phenylhydrazides were recovered which from solution in 100 cc. of absolute alcohol yielded 2.91[1] g. of *l*-threonic phenylhydrazide. The combined crops of phenylhydrazide, 18.09 g., were decomposed by 25 g. of crystallized barium hydroxide in 200 cc. of water by heating on a boiling water bath for 8 hours.[2] There were recovered 9.63 g. of gum of which 8.67 g. (—27.7°) dissolved in ethyl acetate. Attempts to obtain *l*-threonic γ-lactone from this gum were unsuccessful and it was converted into brucine salts by the use of 32 g. of brucine. The crude brucine salts yielded from solution in alcohol three crops of salts, 34.45 g., all in all, melting from 202–206° with $[\alpha]_D^{20} = -25.92°$ to —29.85°. These salts were decomposed by barium hydroxide and gave back 25.12 g. of brucine and 7.9 g. of stiff gum from which no crystalline lactone could be obtained by solution in acetone or in ethyl acetate. The recovered gum possessed $[\alpha]_D^{20} = -29.67°$. Treated with 1.3 cc. of phenylhydrazine, 1.16 g. of the gum yielded 1.25 g. of *l*-threonic phenylhydrazide. The rest of the gum, 6.59 g., in aqueous solution dissolved 2.9 g. of calcium carbonate. After distillation *in vacuo* the gummy calcium salt was dissolved in an equal weight of water, precipitated in a porcelain dish by alcohol and rubbed with a pestle until crystalline. The air-dried calcium *l*-threonate weighed 9.6 g. and lost 0.87 g. of water by drying over sulfuric acid *in vacuo*.

Calc. for $Ca(C_4H_7O_5)_2.3H_2O$: loss of 2 H_2O, 9.89. Found: H_2O, 9.06. 0.4098 g. of salt dried *in vacuo* gave 0.0681 g. of CaO. Calc. for $Ca(C_4H_7O_5)_2.H_2O$: Ca, 12.19. Found: Ca, 11.87. Also 0.5064 g. of salt dried *in vacuo*, dissolved in 12.1881 g. of water, gave $\alpha = -0.30°$ in a 10 cm. tube; $[\alpha]_D^{20} = -7.43°$.

gums 2.1 g. and 4.95 g. were combined and extracted with ethyl acetate; 4.6 g. of gum (—3.47°) were dissolved, leaving 2.15 g. of gum (+4.65°). Brucine salts prepared from the last gum yielded from alcoholic solution 2.63 g. of salts, melting between 195° and 200°; a second crop of salt, 0.36 g. (m. p. 160, $[\alpha]_D^{20} = -28.23°$), had properties like those of brucine *d*-lyxonate (cf. *Ann.*, 403, 249), but it was united again with the gummy salts making 5.86 g. The tarry gums were combined and acetylated with acetic anhydride. The excess of anhydride was removed by distillation *in vacuo*. The acetylated gum was extracted with ether and the ether-soluble portion was saponified with barium hydroxide yielding 0.63 g. of gum.

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[1] The alcoholic filtrate gave back 27.1 g. of gummy phenylhydrazides. The gum recovered from these yielded *d*-erythronic γ-lactone.

[2] The phenylhydrazine was extracted from the cooled, alkaline solution with ether. The barium was removed by sulfuric acid and the gum recovered by distillation *in vacuo*.

After being dried at 100–110° for 16 hours, 2.0536 g. of salt dried in a vacuum lost 0.1297 g. of water. The salt became light brown in color and hygroscopic. On the basis of these analyses the total salt, 9.6 g., contained 1.4214 g. of water crystallization.

Calc. for $Ca(C_4H_7O_5)_2.3H_2O$: H_2O, 14.83. Found H_2O, 14.80.

***d*-Erythronic γ-Lactone.**—The 27.1[1] g. lot of gummy phenylhydrazides were decomposed by barium hydroxide in the usual way. Of the recovered gum amounting to 14.5 g., 3.15 g. were tarry matter (discarded) and 11 g. of gum soluble in boiling ethyl acetate (500 cc.). From the latter boiling ether (500 cc.) extracted 5.77 g. (—18.02°) leaving 4.68 g. (—9.7°). The aqueous solution of the latter gum was treated with 17 g. of brucine and that of the former with 23 g. From both lots of brucine salts six crops of crystalline salts were obtained (from alcoholic solution) amounting to 32.47[2] g. melting from 202–211° with $[\alpha]_D^{20}$ = —26.83° to —27.7°. The combined crops were digested with 300 cc. of absolute alcohol and 24.47 g. of brucine salts melting from 210–212° remained insoluble. The alcoholic filtrate yielded 1.95[3] g. more. On decomposition with barium hydroxide the combined crops, 26.42 g., gave back 20.9 g. of brucine and 5.74 g. of gum (—20.9°). The low rotation of this gum indicated the presence of much *d,l*-glyceric acid and therefore the gum was converted again into brucine salts, 28.98 g., which yielded from solution in a mixt. of 13 cc. of water and 130 cc. of absolute alcohol 11.13 g. of brucine salts melting at 212° with $[\alpha]_D^{20}$ = —28.2°. A second crop of salt, 8.44 g., a small third crop and 5.85 g. of brucine salts, melting at 204°, were combined and recrystallized from solution in a mixture of 7 cc. of water and 70 cc. of absolute alcohol, whereupon 6.6[4] g. of brucine salts, melting at 209° with $[\alpha]_D^{20}$ = —27.02°, were obtained.

The brucine salts, 11.13 g. and 6.6 g., were combined and decomposed by barium hydroxide. The recovered gum, 3.85 g. (—24.75°), was treated with 4 cc. of phenylhydrazine and 4 cc. of absolute alcohol, whereupon 1.57 g. of *l*-threonic phenylhydrazide melting from 149–154° were obtained.

From the alcoholic filtrate 5.08 g. of gummy phenylhydrazides were obtained which, on decomposition with barium hydroxide, gave 2.18 g. of gum, soluble in ethyl acetate, and 0.5 g. of tarry gum. The aqueous solution of the former dissolved 5.3 g. of strychnine and the crude salts, recovered by distillation *in vacuo*, yielded, from solution in absolute

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[1] Cf. footnote, page 1647.

[2] The alcoholic filtrates yielded 10.92 g. of gummy brucine salts.

[3] The alcoholic filtrate yielded 5.38 g. of brucine salts which on decomposition with barium hydroxide gave back 1.12 g. of gum (—8.92°).

[4] The alcoholic filtrate gave back 7.42 g. of gummy brucine salts.

alcohol, 1.71[1] g. of crude strychnine *d*-erythronate melting at 176° with $[\alpha]_D^{20} = -20.9°$. This salt gave on decomposition with barium hydroxide 0.44 g. of gum; from solution in ethyl acetate it gave 0.06 g. of *d*-erythronic γ-lactone, melting at 100–5° with $[\alpha]_D^{20} = -68.9°$, that is, 0.0585 g. dissolved in 3.1235 g. of water gave $\alpha = -0.32°$ in a 2.5 cm. tube; $d = 1.011$.

Calcium Glycollate.—Strychnine salts were prepared from each of the gums 4.41 g.[2] and 4.6 g. The alcoholic solution of the salts from the former yielded 12.85[3] g. and the solution of the salts from the other 10.81[3] g. of crude strychnine glycollate, melting from 140–200°. These salts were combined and decomposed by barium hydroxide. The aqueous acid solution, recovered after removing barium, dissolved 2.67 g. of calcium carbonate.[4] From concentrated aqueous solutions several crops of crystalline calcium glycollate, amounting to 4.9422 g., were obtained. This salt was equivalent to 2.867 g. of glycollic acid.

(I) 3.1906 g. of salt lost 0.9142 g. of water at 100–105°. (II) 1.7160 g. of salt lost 0.4806 g. of water at 100–105°. 0.3570 g. of dried salt gave 0.1052 g. of CaO.

Calc. for $Ca(C_2H_3O_3)_2.4H_2O$: H_2O, 27.48. Found: H_2O, (I) 28.64, (II) 28.00.

Calc. for $Ca(C_2H_3O_3)_2$: CaO, 29.47. Found: CaO, 29.47.

Calcium *l*-Glycerate.—The gummy brucine salts,[5] 16 g., 5.86 g. and 10.92 g., united and decomposed by barium hydroxide, gave back 21.69 g. of brucine and 6.75 g.[6] of stiff gum from which 3.25 g. of good gum (—6.03°) were obtained. This gum was united with 1.12 g. of gum (—8.92°) and the whole converted into brucine salts. The crude salts, 25.6 g., yielded from solution in alcohol 5.85 g. of salts melting at 204°.[7] A second crop of salt[3] was united with a corresponding crop[8] from 7.42 g.

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[1] The gummy strychnine salts recovered from the mother liquor gave back on decomposition with barium hydroxide 1.75 g. of gum.

[2] Cf. footnote, page 1646.

[3] The alcoholic filtrates yielded 7.3 g. and 7 g. of gummy strychnine, respectively. The gums recovered from them combined with 0.63 g. of gum (cf. footnote, page 1646) together amounted to 4.73 g. (—4.44°); this was converted into brucine salts. From solution in alcohol these salts gave 5.4 g. melting from 195–200° which were included in the 114.08 g. lot. The gummy salts, recovered from the filtrate, 16 g., were used later.

[4] No calcium oxalate was found in the undissolved calcium carbonate.

[5] Cf. footnotes, pages 1646 and 1649.

[6] By means of boiling ether 2.7 g. of gum were extracted. The residue was acetylated with acetic anhydride. The excess of anhydride was distilled off *in vacuo* and the acetylated gum was extracted with ether. This ether solution yielded 1 g. of gum which after saponification yielded 0.55 g. of gum which was combined with 2.7 g. making 3.25 g.

[7] For use cf. page 1649.

[8] The gummy brucine salts, recovered from the alcoholic filtrates, were combined, 18.7 g., and decomposed with barium hydroxide. The aqueous solution, after removing barium, contained 3.3 g. of gum (—2.42°) and was evaporated on a boiling water bath, whereby 0.6 g. of glycollic acid was volatilized, leaving 2.68 g. of gum, which was converted into quinine salts; these yielded from aqueous solution 0.22 g. of quinine *l*-glycerate.

of gummy brucine salts[1] making 8.65 g. of crystalline salts melting from 200–208°. These salts gave back, on decomposition with barium hydroxide, 1.8 g. of gum (—13.33°) which on treatment with phenylhydrazine yielded no crystalline phenylhydrazide. The gum, recovered by decomposition of the gummy phenylhydrazides by barium hydroxide, and weighing now 1.3 g., was converted into quinine salts, 5.4 g., which yielded, from solution in 15 cc. of absolute alcohol and by seeding, 1.67 g. of salt melting from 167–176°. Another lot of quinine salts, 6.75 g., prepared from 1.75 g. of gum,[2] yielded 1.79 g. of salts melting from 164–173° which, recrystallized from three parts of absolute alcohol, gave 1.63 g. of salt melting at 162° with $[\alpha]_D^{20} = -114.9°$. The combined quinine salts, 1.67 g. and 1.63 g., recrystallized from 30 cc. of absolute alcohol, gave 1.55 g. of quinine *l*-glycerate melting at 177° with $[\alpha]_D^{20} = -119.9°$. On decomposition with barium hydroxide, this salt yielded 0.36 g. of inactive gum. The calcium salts, prepared from this gum, yielded 0.37 g. of calcium *l*-glycerate melting at 138° with $[\alpha]_D^{20} = +12.1°$.

***l*-Xylose and Cupric Hydroxide.**—The oxidation of 100 g. of *l*-xylose with cupric hydroxide in alkaline solution was carried out in exactly the same way as that of 100 g. of *l*-arabinose. After acidification with hydrochloric acid traces of copper were removed from the solution by hydrogen sulfide. The aqueous solution was distilled *in vacuo*. A very mobile gum, 100.5 g., containing hydrogen chloride, was extracted from potassium sulfate and chloride (which amounted to 750 g.) by alcohol. The gum, recovered by distillation *in vacuo*, was extracted with boiling either (3000 cc.). After concentration to 2000 cc., 26.2 g. of gum (+7.06°), called gum "A," remained in solution, while 1.74 g. of insoluble gum were united with the main lot of gum. From this gum boiling ethyl acetate (500 cc.) extracted 18.5 g. of gum (+27°), called gum "B." The residue, 35.5 g., was treated with 3 cc. of concentrated hydrochloric acid. After distillation *in vacuo*, the gum, 31.95 g. (+34.95°), was separated from potassium chloride by extraction with absolute alcohol. From this gum ethyl acetate extracted 21.57 g. (+48°). The residue, 8.45 g., was freed from potassium salts by hydrochloric acid (2 cc.) and then, after distillation *in vacuo*, 5.45 g. (+49.9°) were extracted by acetone; this gum was combined with 21.57 g. and gave 27.02 g., called gum "C."

***l*-Xylonic γ-Lactone.**—Gum "B," 18.5 g., was resolved by boiling ether (1000 cc.) into 8.1[3] g. of soluble gum (+13.33°) and 9.2 g. of insoluble gum (+44.6°). The latter was added to gum "C" making 36.22 g. of gum with $[\alpha]_D^{20} > +45°$. To the aqueous solution of this gum 40 g. of hydrobromic acid (sp. gr. 1.49) were added and in this solution 40.1 g.

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[1] Footnote, page 1649.

[2] Cf. p. 1648.

[3] Glycollic acid was found in this.

of cadmium carbonate dissolved. On concentration 33.46 g. of a double salt of cadmium *l*-xylonate and cadmium bromide,[1] $Cd(C_5H_9O_6)_2.CaBr_2.2H_2O$, with $[\alpha]_D^{20} = +6.77°$, separated out. A second crop of 8.72 g. was obtained after concentration of the filtrate. The aqueous solution of the combined crops of double salt was freed from cadmium by hydrogen sulfide and from hydrobromic acid by silver carbonate. After distillation *in vacuo*, 16.4 g. of gum were obtained, of which 15.5 g. dissolved in acetone. From this solution 3.4 g. of *l*-xylonic γ-lactone,[1] melting at 96.9° with $[\alpha]_D^{20} = +89.1°$, separated out. On concentration of the filtrates[2] six smaller crops amounting to 6.42 g. and melting from 98–104° were obtained.

***d*-Lyxonic γ-Lactone.**—The uncrystallizable cadmium salts, recovered by distillation *in vacuo* from the filtrates above, weighed 45 g. The cadmium and hydrobromic acid were removed as before. After distillation *in vacuo*, 19 g. of tarry gum were recovered, of which 10.75 g. (+30.45°) dissolved in acetone. From this gum boiling ethyl acetate (100 cc.) extracted 5.45 g. (+19.63°). The insoluble residue,. 5.25 g. (+44.96°), treated with 5 cc. of phenylhydrazine and 6 cc. of absolute alcohol, yielded 3.6 g. of *d*-lyxonic phenylhydrazide, melting at 164° with $[\alpha]_D^{20} = -13.72°$.

From the 5.45 g. lot of gum ether extracted 3.8 g. (+11.05°) leaving 1.6 g. of gum (+41°), which, on treatment with 1.6 cc. of phenylhydrazine and 2 cc. of absolute alcohol, yielded 0.94 g. of *d*-lyxonic phenylhydrazide. The alcoholic filtrates were distilled *in vacuo* and the excess of phenylhydrazine was extracted from the aqueous solution of the phenylhydrazides. After the water had been distilled off *in vacuo*, the phenylhydrazides yielded from alcoholic solution 0.25[3] g. more of *d*-lyxonic phenylhydrazide. The three crops of phenylhydrazide, 4.79 g., on decomposition with barium hydroxide, yielded 2.5 g. of crude lactone gum. From solution in ethyl acetate 1.1 g. of *d*-lyxonic γ-lactone, melting from 92–109°, were obtained in four crops. On recrystallization from acetone these gave 0.43 g. of long needles melting from 104–110° with $[\alpha[_D^{20} = +84.75°$.[4]

Oxalic and Glycollic Acids.—Gum "A," 26.2 g., in aqueous solution, dissolved 47.7 g. of strychnine by heating and the cooled solution yielded 3.81 g. of secondary strychnine oxalate. The filtrate was distilled *in vacuo* and the recovered salts were dissolved in alcohol. From this solution 14.46 g. of strychnine salts, melting from 157–190°, separated out; these were recrystallized from water giving 0.97 g. more of strychnine oxalate. From the aqueous filtrate 13.49 g. of crude strychnine glycollate were recovered. From the alcoholic filtrate (14.46 g. salt having been

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[1] *Ann.*, 403, 253 (1913).

[2] First acetone was used as a solvent and, when no more crystals could be obtained from this solvent, ethyl acetate was used.

[3] The gummy phenylhydrazides were not analyzed further.

[4] *Ann.*, 403, 248–9 (1913).

removed) a second crop of strychnine glycollate, 6.5 g.,[1] melting from 150–195° with $[\alpha]_D^{20} = -25.74°$, was obtained.

The aqueous solution of 8.1 g. of gum (page 1650) dissolved 15.45 g. of strychnine. From the alcoholic solution of the crude salts, 3.6[1] g. of strychnine glycollate, melting from 150–195° with $[\alpha]_D^{20} = -22.1°$, separated out.

On decomposition with barium hydroxide, the combined drops, 6.5 g. and 3.6 g., yielded 7.7 g. of strychnine and 1.9 g. of gum (+13.16°); the crop of 13.49 g. of salt gave 10.95 g. of strychnine and 2.3 g. of gum (+8.7°). By evaporating the aqueous solution of the combined gums on a boiling water bath for 13 hours, 1.7 g. of glycollic acid were expelled leaving 2.5 g. of gum (+22.6°).

From the two crops of secondary strychnine oxalate combined, 4.78 g., 3.9 g. of strychnine and 0.7 g. of oxalic acid crystals were obtained.

Summary.

Oxidation of Arabinose by Air.—The products obtained from 50 g. of substance were: 15.35 g. of formic acid, 3.7313 g. of calcium glycollate, 14.12 g. of *l*-erythronic γ-lactone, 0.68 g. of *d*-threonic phenylhydrazide, 0.33 g. of quinine *l*-glycerate and 0.44 g. of calcium *d*-glycerate.

Oxidation of *l*-Arabinose by Cupric Hydroxide.—The products obtained from 100 g. of substance were 2.92 g. of glycollic acid (volatilized), 1.38 g. of oxalic acid, 2.63 g. of *l*-arabonic γ-lactone.

Oxidation of *l*-Xylose by Air.—The products obtained from 50 g. of substance were 13.17 g. of formic acid, 18.09 g. of *l*-threonic phenylhydrazide, 0.06 g. of *d*-erythronic γ-lactone, 4.9422 g. of calcium glycollate, 0.37 g. of calcium *l*-glycerate.

Oxidation of *l*-Xylose by Cupric Hydroxide.—The products obtained from 100 g. of substance were 6.42 g. of *l*-xylonic γ-lactone, 1.1 g. of *d*-lyxonic γ-lactone, 1.7 g. of glycollic acid (volatilized), and 0.7 g. of oxalic acid.

Chicago, Ill.

[Contribution from the Chemical Laboratory of the University of Michigan.]

TRIPHENYLMETHYL. XXVII. THE MOLECULAR WEIGHTS OF THE TRIARYLMETHYLS.

By M. Gomberg and C. S. Schoepfle.

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It is now generally accepted that the "free radicals" of the triphenylmethane series owe their unique and distinctive character to the presence

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[1] The gummy strychnine salts from the filtrates, on decomposition with barium hydroxide, yielded 19.35 g. of gum from which ether extracted 11.8 (+3.81°). From the insoluble portion ethyl acetate extracted 5.6 g. (+14.16°) leaving 2.25 g. of tarry gum. Brucine salts were prepared from 11.8 g. of gum; from alcoholic solution these yielded 22.77 g. of brucine salts melting from 198–207°.