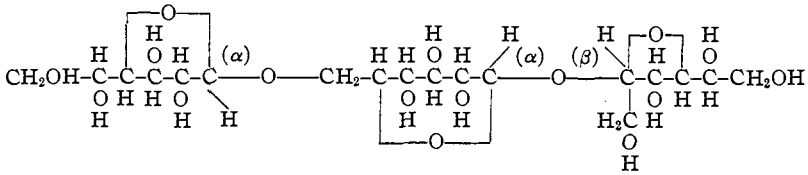
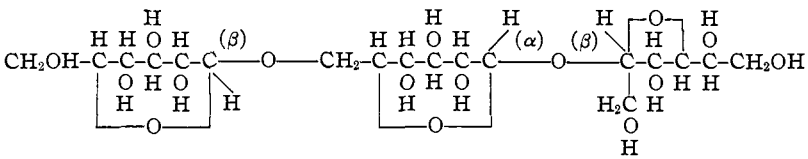


(X) Raffinose



(XI) Gentianose

Postscript of March 4, 1930.—It will be shown in a later article that the rotations of primverose and its beta hepta-acetate agree with the structure 6-[β-*d*-xylosido(1,5)]-*d*-glucose(1,5), that the structure of vicianose is in all probability 6-[α-*l*-arabinosido(1,5)]-*d*-glucose(1,5) and that vicianin is 6-[α-*l*-arabinosido(1,5)]-β-*d*-glucosido(1,5)-*l*-mandelonitrile.

12. Summary

The occurrence of ring shifting during the methylation of some glycosides, as was shown in the preceding article, makes it necessary to determine the structures and configurations of the compound sugars by methods which avoid this disturbing complication. It is shown that the isorotation rules apply closely to the group of compound sugars and that the full structures and configurations of these substances can be determined by the use of these rules in conjunction with other data on structure that are valid whether or not ring shifts occur during methylation. The results give new structures for maltose, melibiose, sucrose, gentianose and raffinose.

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NOTES

A Note on the Preparation of Lecithin.—The preparation of pure lecithin was recently undertaken in order to study the relation of the pure product to the process of blood coagulation.[1]

The method used was that described by Levene and Rolf;[2] a simplification of similar methods previously used by Bergell,[3] McLean[4] and by Levene[5] and his co-workers. It consists in the simple extraction of dried

[1] A. Wadsworth, F. Maltaner and E. Maltaner, *Am. J. Physiol.*, **91**, 423 (1930).

[2] P. A. Levene and I. P. Rolf, *J. Biol. Chem.*, **72**, 587 (1927).

[3] P. Bergell, *Ber.*, **33**, 2584 (1900).

[4] H. McLean, *Biochem. J.*, **9**, 351 (1915).

[5] P. A. Levene and C. J. West, *J. Biol. Chem.*, **34**, 175 (1918); P. A. Levene and I. P. Rolf, *ibid.*, **46**, 353 (1921).

tissue with ethyl alcohol, the chilling out of fats at 0°, precipitation of the lecithin as the cadmium salt, purification of the cadmium salt by exhaustive extraction with ether and recovery of the lecithin by treatment of a chloroform solution of the cadmium salt with a saturated methyl alcohol solution of dry ammonia gas, the recovered lecithin being purified further by emulsifying an ether solution in 10% acetic acid and reprecipitating with acetone.

Considerable difficulty was encountered in the precipitation of the cadmium salt. This was found to be due to the use of absolute methyl alcohol in the preparation of the cadmium chloride solution used for precipitation.

It was found after a considerable loss of time and material that a good yield of a satisfactory cadmium lecithin compound could only be obtained by the use of moist (95%), instead of absolute, methyl alcohol for this step of the procedure.

It was further observed that a pure product could be obtained without recourse to the final purification with acetic acid. This acetic acid treatment decreases the yield greatly and tends to darken the product.

It was possible, moreover, to recover a considerable quantity of pure lecithin from the fats originally precipitated at 0° from the alcoholic extracts of tissue by extraction with alcohol at 0° and subsequent precipitation with the 95% methyl alcohol solution of cadmium chloride.

The results obtained in the preparation of lecithin from beef liver and beef heart are tabulated below.

TABLE I

ANALYSIS OF LECITHIN

Lecithin	Carbon, %	Hydrogen, %	Nitrogen, %	Amino Nitrogen, %	Phosphorus, %
Liver lecithin (one acetic acid treatment)	65.18	10.38	1.94	0.005	3.90
Liver lecithin (no acetic acid used)	65.50	10.69	1.82	0.004	3.84
Liver lecithin (recovered from acetone washings)	64.62	10.51	1.72	...	3.84
Heart lecithin (no acetic acid used)	64.66	11.14	2.06	0.000	3.87
Oleic–stearic lecithin (calcd.)	65.55	11.01	1.73	0.000	3.85
Oleic–palmitic lecithin (calcd.)	64.81	10.81	1.80	0.000	3.99

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Isolation of an Arsenic Compound of Pyridine and Some Observations Concerning the Phase System Arsenic Trichloride–Pyridine.—During the past twenty years many articles have appeared describing reactions that take place between pyridine and inorganic salts. Most of the studies that have been made in this country trace back, directly or indirectly, to Dr. L. Kahlenberg. The studies have usually been accompanied by phase rule interpretations.

In so far as the author knows, no study has been made of the system arsenic trichloride–pyridine, though evidence of reaction between these compounds is recorded in the well-known studies of P. Walden.[1] Walden predicted from conductivity studies that a compound containing one molecule of pyridine and one molecule of arsenic trichloride was formed from interaction between these chemicals, but he made no attempts to isolate or describe any of the properties of such a compound. While a compound of the formula predicted by Walden was not isolated in this work, a compound giving the theoretical arsenic content for the compound $AsCl_3 \cdot 2C_5H_5N$ was isolated.

Experimental.—The best grade of pyridine produced by Kahlbaum was distilled from potassium permanganate, then from fused barium oxide and the fraction coming over between 114.9 and 115.3° at 750 mm. was stored over recently fused potassium hydroxide. Arsenic trichloride of C. P. grade was distilled from recently sublimed metallic arsenic. Upon taking an excess of the purified pyridine (*i. e.*, about 75 mole per cent.), and thoroughly mixing it in a dry container with the prepared arsenic trichloride, there was much heat evolved. Upon cooling in a dry atmosphere distinct rosets of crystals were produced. These crystals were freed from mother liquor by thorough centrifuging. Since the crystals were highly hygroscopic, it was impractical to wash them free of mother liquor by use of organic solvents. The compound was analyzed for arsenic by decomposing it with alkali and titrating with iodine solution. The iodine solution had been carefully standardized against arsenious acid made up from purified and resublimed arsenious oxide. The following analyses were obtained: Sample I, As, 22.11%; II, 21.91%; III, 22.16%. The theoretical amount of arsenic in the compound $AsCl_3 \cdot 2C_5H_5N$ is 22.08%.

Phase rule applications to this system are particularly difficult due to undercooling and to tendency toward obtaining abnormal time–temperature cooling curves. While an arsenic trichloride–pyridine mixture of 66.67 mole per cent., with reference to pyridine, gives a distinct freezing point rise, roughly fixing the melting point for the compound $AsCl_3 \cdot 2C_5H_5N$ at 64°, the curve may or may not be continuous in its rise.

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[1] P. Walden, *Z. physik. Chem.*, **43**, 445 (1903).

The Preparation of Acetylchloro-aminobenzene.—The physical and chemical properties and the rate and mechanism of the rearrangement of acetylchloro-aminobenzene have been investigated recently in several laboratories.[1] Since the presence of impurities such as acetanilide affect the rearrangement in aqueous solution[1c,2] and in glacial acetic acid,[1c,2] it is desirable to have a method of preparation which will produce acetylchloro-aminobenzene without contamination with other anilides. A method is outlined below which can be relied upon to give a 70% yield of pure acetylchloro-aminobenzene melting at 91° and requiring no further purification.

(A) To a solution of 15 g. of acetanilide (0.11 mole) in 3 liters of water, 16.8 g. of sodium bicarbonate (0.2 mole) is added and the whole is filtered to remove suspended particles.

(B) To 150 cc. of 1.0 *M* sodium carbonate chlorine gas is added until the solution contains between 1.6×10^{-3} and 1.8×10^{-3} equivalents of chlorine per cc. as determined by analysis of a portion. This is prepared at 5° and the solution is filtered before using.

Solution A is kept at approximately 5° and is stirred slowly by a mechanical device during the dropwise addition of a calculated volume of Solution B. (Too rapid stirring of A may cause precipitation of acetanilide.) The product, acetylchloro-aminobenzene, precipitates toward the end of the addition of the chlorine solution. After standing for about fifteen minutes to insure complete precipitation, the needle-like crystals are removed by filtration, washed with cold water until no further test for chloride ion is obtained and dried at room temperature in a vacuum desiccator over sulfuric acid; yield, 13 g., melting point 90.5–91°.[3]

The product may be recrystallized from a solvent composed of 1 part of acetone and 9 parts of petroleum ether, yielding plate-like crystals which have the same melting point as the needles.

Armstrong[4] prepared the substance at elevated temperatures. (50–85°) and obtained fine needles. Chattaway and Orton[5] replied to his statement as to the crystal form as follows: "Acetylchloro-aminobenzene, from whatever solvent it separates, crystallizes, according to our observations in plates or short, four-sided prisms. When needles are present, they are undoubtedly the isomeric *p*-chloro-acetanilide. . . . . " The discovery that the compound may be prepared in either form settles a dispute of long standing.

The method here presented differs from others in use up to the present time in that a sodium bicarbonate buffer is present in the acetanilide solution, which prevents the formation of *o*- and *p*-chloro-acetanilide even

[1] (a) Mathews and Williamson, THIS JOURNAL, **45**, 2574 (1923); (b) Orton, Soper and Williams, *J. Chem. Soc.*, 998 (1928); (c) Soper, *J. Phys. Chem.*, **31**, 1193 (1927); (d) Bradfield, *J. Chem. Soc.*, 351 (1928); (e) Porter and Wilbur, THIS JOURNAL, **49**, 2145 (1927).

[2] Porter and Barnes, paper ready for publication.

[3] Since the compound decomposes on heating, samples should be placed in the bath, which is already at 82–83°. Then with the usual rate of heating, the product, if pure, will melt at 90.5–91°.

[4] Armstrong, *J. Chem. Soc.*, **77**, 1047 (1900).

[5] Chattaway and Orton, *ibid.*, **79**, 274 (1901).

though a chlorine solution is used which is three times the maximum concentration considered safe by Chattaway and Orton.[6] The method is rapid and the product is better than 99.7% pure.

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Note on Caryophyllin and Urson.—In a previous article[1] the writer reported the results of an examination of caryophyllin and urson, two very similar and probably isomeric compounds, having apparently the composition $C_{30}H_{48}O_3$ and exhibiting properties which could best be explained by the assumption of an oxy-lactone structure, or the grouping $\left\{\begin{matrix}-OH\\-O-\\-CO-\end{matrix}\right]$

More recently urson has been studied by van der Haar,[2] who has arrived at the conclusion that the alternative formula, $\left\{\begin{matrix}-OH\\-COOH\end{matrix}\right.$, which is that of an hydroxy acid, has been demonstrated. The arguments against this formula have already been noted by the writer. Van der Haar also criticizes the methods employed by the writer as "uncontrolirbar" in comparison with elementary analyses, but in reality, the titrations used to show the functional relations of these compounds can be "controlled" or checked with the utmost ease, and they were employed exactly because they are more conclusive and satisfactory for the purpose in view than combustions.

It was found that caryophyllin and urson could be titrated with accuracy in alcoholic solution, the results indicating one carboxyl or lactone group in the C_{30} molecule. On acetylation, two acetates were obtained; one, an unstable diacetate, convertible by boiling with alcohol into a stable mono-acetate, which in turn yielded the original caryophyllin or urson by hydrolysis with alkali. These results appeared to be explainable only by the oxy-lactone formula. Van der Haar, however, obtained from urson an acetate, melting at 200°, which on boiling with alcohol gave a compound melting at 275°, which without further examination he assumed to be urson. Inasmuch as urson melts at about 285° and the mono-acetate at about 265°, the identification is rather unsatisfactory. In view of the importance of this fact for his hypothesis, a more thorough examination of the product would have been desirable. A quantitative hydrolysis would have been conclusive. In two later articles[3] van der Haar has revised his previous

[6] Chattaway and Orton, *J. Chem. Soc.*, **75**, 1046 (1899).

[1] Dodge, THIS JOURNAL, **40**, 1917 (1918).

[2] Van der Haar, *Rec. trav. chim.*, **43**, 367, 542 (1924).

[3] Van der Haar, *ibid.*, **46**, 775 (1927); **47**, 585 (1928).

conclusions and, employing the methods used by the writer finds, in fact, that caryophyllin (which is shown to be identical with the sapogenin of beets, and also with the oleanol of Power and Tutin)[4] yields two acetates. Urson also gave two similar derivatives.

To reconcile these facts with the hydroxy acid formula, which permits but one acetyl derivative, he suggests for the compound described by the writer as diacetate, the formula $[C_{30}H_{48}(OAc)CO]_2OAc_2O$, which represents the anhydride of the acetylated hydroxy acid combined with one molecule of acetic anhydride "of crystallization!" On treatment with alcohol this is supposed to yield the monoacetate, $C_{30}H_{48}(OAc)COOH$.

It is hardly necessary to point out the anomalous nature of this hypothesis. If the first compound is really a molecular compound of an acid anhydride with acetic anhydride, boiling with alcohol should, by all analogy, yield an ester, and not the free acid. To the writer, the lactone formula appears less involved in difficulties.

Van der Haar also claims to have "proved," from the results of two combustions, the formula of urson to be $C_{31}H_{50}O_3$, instead of the previously accepted $C_{30}H_{48}O_3$. How much importance should be ascribed to this is not clear. Equally good analyses may be cited for the latter formula. It is to be noted, however, that Power and Tutin found the composition $C_{31}H_{50}O_3$ for oleanol (probably identical with caryophyllin) and prunol (apparently identical with urson), thus agreeing with van der Haar. The former also described two acetates of oleanol, and considered it to be a phenol. Yet this assumption, as well as the hydroxy acid hypothesis, seems to be contradicted by the insolubility of these compounds in aqueous alkali. Furthermore, both compounds show an unusual stability at high temperatures. They may be sublimed without decomposition: caryophyllin, in fact, is slowly volatile in steam, and has been frequently observed by the writer as an almost pure sublimate on the covers of stills used for the extraction of oil of cloves. This stability seems to the writer to indicate very definitely the lactone structure. Compare, for example, *o*-coumaric acid, a typical hydroxy acid, which decomposes at its melting point, and its lactone, coumarin, which distils without decomposition at 280°.

To sum up, the question as to the elementary composition of these compounds may be considered as open, with the evidence rather in favor of the C_{30} formula. As to the functions of the oxygen atoms, the writer is still of the belief that the lactone formula is the only one available.

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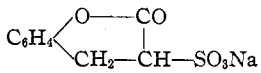
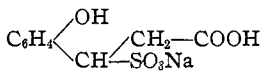
[4] Power and Tutin, *J. Chem. Soc.*, **93**, 891 (1908).

Some Derivatives of Coumarin. II.—The reaction of coumarin with acid sulfite solutions was found by the writer[1] to result in the formation of sulfonic derivatives of hydrocoumarin, the sodium salt, for example, having the composition $NaSO_3C_9H_7O_2 \cdot H_2O$, and probably the structure



More recently, Dey and Row[2], by treating coumarin with sodium sulfite and subsequent acidification, obtained a salt $NaSO_3C_9H_9O_3 \cdot H_2O$, to which they assigned the structure



Inasmuch as the writer had not previously observed the occurrence of an acid salt of this type, and Dey and Row make no reference to the lactone salt already described, it seemed desirable to repeat some of this work in order to characterize more exactly the salt or salts in question. The result of the examination has confirmed the previous work of the writer, and also, to a certain extent, that of Dey and Row.

The lactone salt is obtained by treating coumarin with a solution of sodium acid sulfite. It crystallizes in flat prisms with rectangular ends, under the microscope apparently orthorhombic. The crystals effloresce at the ordinary temperature, and are soluble in about five parts of water at 20°. The fresh solution is neutral to litmus and gives no color with ferric chloride. Addition of salt to the solution precipitates the lactone salt almost completely.

The acid salt is readily prepared as follows: coumarin (20 g.) is dissolved, by moderate heating, in about 100 g. of sodium sulfite solution (25% $Na_2SO_3 \cdot 7H_2O$). If the solution becomes alkaline to phenolphthalein, it may be neutralized with acid sulfite. When all the coumarin is dissolved, the solution is filtered, diluted to about 160 g., 35 cc. of about 4 *N* hydrochloric acid added and the mixture allowed to crystallize in the cold, or, if large crystals are desired, by slow evaporation at the ordinary temperature.

The acid salt is deposited in large transparent prisms with pyramidal terminations, or, more rarely, in rhombic prisms with basal planes. Sections perpendicular to the prism faces show in convergent polarized light the characteristic interference figure of orthorhombic crystals. The crystals contain $3H_2O$, do not effloresce and are soluble in about three parts of water at 20°. The solution is strongly acid and is not precipitated by the addition of salt.

[1] Dodge, THIS JOURNAL, **38**, 446 (1916).

[2] Dey and Row, *J. Chem. Soc.*, **125**, 554 (1924).

Anal. 2.00 g. at 105–110° lost 16.63%, 2.001 g. lost 16.55% of water. Calcd. for $3H_2O$: 16.77%. *Titration.* Subs., 1.998, 1.667, 1.4365: 12.4, 10.8, 9.0 cc. of 0.5 *N* KOH. Calcd. acid value: 170.8. Found: 173, 181, 175. Subs., 1.998: Na_2SO_4, 21.4%. Calcd.: 22%.

The slightly high acid values are probably due to the phenolic hydroxyl, as similar high values are obtained in titrating coumaric acid.

The writer was unable to obtain the monohydrated salt described by Dey and Row. In several batches, however, the large prisms were accompanied by groups of silky needles, which could not be readily purified; these also often appear in recrystallizing the pure trihydrate.

With ferric chloride solution the acid salt gives a very characteristic bright blue coloration. A *fresh* solution of the lactone salt shows, as already stated, no color with this reagent. If, however, the solution is allowed to stand, after a few hours a greenish-blue color is obtained, and after twenty-four hours, a bright blue, indistinguishable from that of the acid salt. This indicates that the lactone salt, in solution, is gradually hydrolyzed to the acid salt, which is exactly what would be expected. For the hydrocoumarin ring, being a saturated δ-lactone, has no longer the characteristic stability of the coumarin ring, but in solution tends to an equilibrium between lactone and acid.

Excess of mineral acid throws the equilibrium point toward the lactone stage, which explains the fact that from the mother liquor of the trihydrate acid salt, some lactone salt can be obtained by salting out.

Very strong acid causes a partial hydrolysis to coumarin. For example, 10 g. of concentrated hydrochloric acid was added to a solution of 6 g. of acid salt in 10 g. of warm water and the mixture evaporated to dryness. On dissolving the residue in 30 cc. of water, 0.8 g. of coumarin remained; the filtrate on addition of salt gave an abundant precipitate of lactone salt.

On heating above 120°, the acid salt, like the lactone salt, yields coumarin.

Summary.—From coumarin, by addition of sodium bisulfite, two distinct salts are obtained: one, a lactone corresponding to hydrocoumarin, the other an acid salt corresponding to hydrocoumaric acid.

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