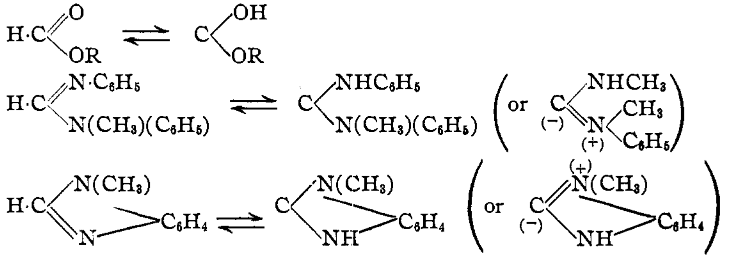
disprove the existence of the tautomerism between the derivatives of formic acid and carbonous acid represented in the equations



It was hoped that the hydrogen atoms in the "carbonous acid" formulas on the right would be sufficiently acidic to react with the metallic amides in liquid ammonia to form salts which would clearly show the reactions of derivatives of divalent carbon. No such expectations were realized, because of the more pronounced tendency of the metallic amides to add to the double bond between the carbon and nitrogen, of compounds represented by the two lower formulas in the left-hand column.

2. Ethyl formate is not converted to a potassium salt by the action of potassium amide in liquid ammonia, nor is formic acid converted to a dipotassium salt.

3. Only one hydrogen atom of benzimidazole can be replaced by a metal in liquid ammonia, in agreement with the accepted formula.

STANFORD UNIVERSITY, CALIFORNIA

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The Composition of Lemon Albedo Pectin[1]

BY CATHERINE M. BRIDGHAM AND C. G. KING

Substances containing sugars combined with uronic acids have lately been found to occur widely, comprising the chief structural material of plant gums, mucilages, hemicelluloses, pectins, bacterial gums, etc. Their biological and industrial importance clearly justifies intensive study of their chemical nature. The recent identification of vitamin C as a six-carbon sugar acid[2] has added to the interest in this group of substances. Lemon pectin has become an important commodity in the recovery of by-products from the citrus fruit industry.

Identification of Structural Units.—Fresh lemon albedo (white portion of peel) was partially purified by alcohol and ether extraction, after which the pectin was ex-

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[1] This paper is based upon a thesis submitted by Catherine M. Bridgham to the Graduate School of the University of Pittsburgh in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Waugh and King, *J. Biol. Chem.*, **97**, 325 (1932); *Science*, **75**, 357 (1932); *ibid.*, **76**, 630 (1932); Svirbely and Szent-Gyorgi, *Biochem. J.*, **26**, 865 (1932); *Nature*, **129**, 576 (1932).

tracted from the albedo by water. The pectin was precipitated from solution by the dropwise addition of 95% alcohol in the presence of 0.1% sodium chloride. The flocculent precipitate was filtered, redissolved in water, reprecipitated, and dried in a vacuum desiccator at room temperature. Air-dried albedo yielded about 13% of its weight as pectin by cold water extraction and an additional 2% by water extraction at 70°.

Methoxyl group determinations (methanol was identified by the United States Pharmacopoeia test) were made by both the Zeisel and the Nanji and Norman[3] methods. The Zeisel method should give total methoxyl groups, the Nanji and Norman method should give only those combined in ester formation. The average values were 9.94% by the Zeisel method and 11.30% by the Nanji and Norman method. Therefore, it appeared unlikely that any methoxyl groups were present in other than ester-type combination.

The pectin was subjected to hydrolysis with 3% sulfuric acid for fifteen hours at 100°, or for five hours in an autoclave at fourteen pounds pressure. Barium galacturonate was obtained from the hydrolysate by the method of Link and Nedden.[4] When purified, it was found to contain 26.32% barium (theoretical 26.25%). After the barium was removed from a sample of barium galacturonate by addition of dilute sulfuric acid, *d*-galacturonic acid was identified by the preparation of a brucine salt as described by Ehrlich and Schubert.[5] The salt melted at 180–183° (reported, 180°).

The sugar units were identified in the alcoholic filtrate after separation from barium galacturonate. The solution was evaporated to a very small volume under reduced pressure at 35°, and again treated with barium carbonate to ensure complete removal of all galacturonic acid. The solution was again evaporated under reduced pressure, and the slight trace of colored matter removed by warming the solution with powdered charcoal. From the colorless filtrate, mixed phenyl osazones were prepared. The hot-water-soluble osazone melted at 160°, and its mixed melting point with *l*-arabinosazone (prepared from the pure sugar) was 160°. The alcohol-soluble osazone melted at 195° (mixed melting point with *d*-galactosazone, prepared from the pure sugar, 194–195°). Galactose was further identified by isolating mucic acid after oxidation of the sugar solution (free from galacturonic acid) with nitric acid.

Relative Amounts of *d*-Galacturonic Acid, Arabinose, Galactose, and Methanol.—Barium pectate was prepared by warming pectin with 1% sodium hydroxide solution for an hour, neutralizing with hydrochloric acid, filtering off the pectic acid, dissolving in a large volume of distilled water, and adding barium hydroxide solution to the solution of pectic acid (until neutral to Congo red). The gelatinous barium pectate, after purification, was dried at 110° to constant weight. It contained 21.03% barium.

The furfural (precipitated with thiobarbituric acid according to the method of Wise and Peterson[6]) and mucic acid yields from barium pectate and from barium galacturonate, the furfural yield from *l*-arabinose, and the mucic acid yield from *d*-galactose, together with the barium content of the two salts (pectate and galacturonate), permitted calculation of the relative amounts of barium galacturonate, arabinose, and galactose in barium pectate. The calculations were based upon the anhydride forms of the constituents.

Based upon the figures given in Table I, the following calculations were made: (1) barium galacturonate anhydride in barium pectate, (21.03/27.26)100 = 77.15%; (2) furfural due to the anhydride, 0.7715 × 7.07% = 5.45%; (3) furfural due to anhydro-arabinose, 9.33% − 5.45% =

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(3) Nanji and Norman, *J. Soc. Chem. Ind.*, **45**, 337T (1926).

(4) Link and Nedden, *J. Biol. Chem.*, **94**, 307 (1931).

(5) Ehrlich and Schubert, *Ber.*, **62**, 1974 (1929).

(6) Wise and Peterson, *Ind. Eng. Chem.*, **22**, 362 (1930).

TABLE I

EXPERIMENTAL QUANTITATIVE YIELDS (WITH ANHYDRIDE EQUIVALENTS IN PARENTHESES)

Unit	Barium, %	Furfural, %	Mucic acid, %
Barium galacturonate	26.32 (27.26)	6.83 (7.07)	41.34 (42.81)
Arabinose		36.79 (39.14)	
Galactose			61.29 (64.52)
Barium pectate	21.03	9.33	40.98

3.88%; (4) anhydro-arabinose in barium pectate, 3.88%/0.3914 = 9.91%; (5) mucic acid due to barium galacturonate anhydride, 0.7715 × 42.81% = 33.03%; (6) mucic acid due to anhydro-galactose, 40.98% − 33.03% = 7.95%; (7) anhydro-galactose in barium pectate, 7.95%/0.6452 = 12.32%; (8) total accounted for, 99.38% of the barium pectate. The corresponding molar ratios would be approximately (for pectic acid) 4 galacturonic acid:1 arabinose:1 galactose.

The average minimum equivalent weight, by sodium hydroxide titration of pectic acid, was found to be 255.5. If there were four acid groups, the corresponding molecular weight would be 1022. The calculated molecular weight for pectic acid, if all the units were joined in a closed ring, with the elimination of 6 moles of water, would be 998. If the units were joined in a chain, with the elimination of 5 moles of water, the calculated molecular weight would be 1016.

The average experimental value for the methoxyl content of pectin being 9.94% by the Zeisel method and 11.30% by the Nanji and Norman method (average of all determinations, 10.52%), the evidence indicates that practically all of the galacturonic acid units in lemon albedo pectin were originally present as methyl esters.

The average of seven determinations of the carbon dioxide yield from pectin was 14.83%, but the individual results varied rather widely (theoretical value, 16.42%).

Less vigorous hydrolytic treatments with 3% sulfuric acid, or with 1% oxalic acid, failed to give satisfactory yields of intermediate combinations of galacturonic acid with either galactose or arabinose.

Conclusion.—Our findings for lemon peel pectin are in general agreement with Ehrlich's report[7] for beet pectin, the report of Nanji, Paton and Ling[8] for apple, beet, orange, and onion pectins, and the composition of flax pectin found by Norris.[9] Lemon peel pectin is chiefly the tetramethyl ester of pectic acid. Norman[10] has reported that lemon juice pectin is the tetramethyl ester of pectic acid, but that the methoxyl content corresponded to that of the trimethyl ester in cases where degree of purity had not been considered.

(7) Ehrlich, *Chem.-Ztg.*, **41**, 197 (1917).

(8) Nanji, Paton and Ling, *J. Soc. Chem. Ind.*, **44**, 253T (1925).

(9) Norris, *Biochem. J.*, **23**, 195 (1929).

(10) Norman, *ibid.*, **22**, 749 (1928).

Summary

1. The constituent units of lemon albedo pectin are *d*-galacturonic acid, *l*-arabinose, *d*-galactose and methyl alcohol.

2. The units are present in the approximate ratio of 4 moles of galacturonic acid to 1 mole of arabinose and 1 mole of galactose.

3. The four galacturonic acid units are chiefly present in the native pectin as methyl esters.

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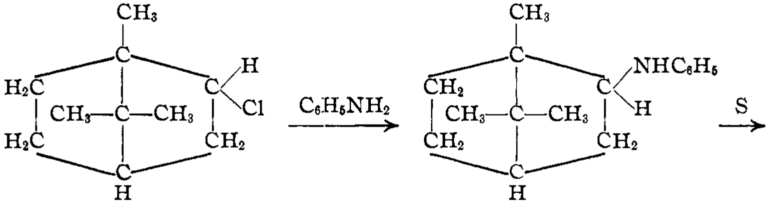
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

A New Camphor Synthesis

BY JOHN J. RITTER

The synthesis of camphor from α-pinene has been intensively studied because of its economic importance. Notwithstanding the voluminous literature on the subject, there appears to be only one practical method, the well-known synthesis through bornyl chloride, camphene, isobornyl acetate or formate, and isoborneol, to camphor.[1] The method suggested here was developed during the study of certain aniline derivatives of the terpenes, on which preliminary reports have already been presented before this Society.[2]

It was observed during these experiments that isobornylaniline obtained by the action of aniline on bornyl chloride[3] underwent dehydrogenation when heated with sulfur to produce camphor anil in good yield. The camphor anil so obtained is identical (with the probable exception of optical character) with the product obtained by Reddelien and Meyn[4] by condensation of aniline with camphor. Camphor anil hydrolyzes rapidly with aqueous acids to camphor and aniline. The new series of transformations is represented as follows



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[1] The present practice in camphor manufacture is fully discussed in O. Aschan, "Die Naphthenverbindungen, Terpene, Campherarten," Walter de Gruyter, 1929, pp. 163–173.

[2] Ritter and Mottern, "The Fixation of Aniline by Hydrocarbons of the Terpene Series," American Chemical Society meeting at Buffalo, N. Y., Sept., 1931; "The Constitution of Bornylaniline," THIS JOURNAL, **54**, 3458 (1932).

[3] Ullmann and Schmidt, *Ber.*, **43**, 3202 (1910).

[4] Reddelien and Meyn, *ibid.*, **53**, 345 (1920).