Derritol, isoderritol, rotenol, dihydroxyrotenonic acid and isodihydroxyrotenonic acid on alkali fusion yielded isotubaic acid.

Rotenonic acid, as well as several other derivatives of rotenone in which the lactone group was opened by catalytic reduction, did not give isotubaic or dihydrotubaic acid on fusion with alkali.

Compounds which gave isotubaic or dihydrotubaic acid contain the lactone group or this group has been opened by hydrolysis. The conclusion is drawn that the hydroxyl group resulting from the opening of the lactone ring is necessary for the formation of isotubaic or dihydrotubaic acid.

The fact that rotenol gives isotubaic acid contradicts the theory that cleavage of the molecule takes place at the ketone group.

The nucleus of tubaic acid does not exist in derritol as such, but is a secondary decomposition product. Perhaps it does not exist in rotenone.

Substance	Product of alkali fusion
Derritol	Isotubaic acid
Isoderritol	Isotubaic acid
Rotenol	Isotubaic acid
Dihydroxyrotenonic acid	Isotubaic acid
Isodihydroxyrotenonic acid	Isotubaic acid
Dehydrorotenone	Isotubaic acid
Dihydroderritol methyl ether	Dihydrotubaic acid
Rotenonic acid	....
Dehydrodihydrorotenonic acid	Unidentified phenolic acid
Dihydrorotenolic acid	Unidentified phenolic acid

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THE COMPOSITION OF SALKOWSKI'S ARABAN

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Introduction

Most of the methods devised in the attempt to prepare pure xylans have involved the use of alkaline copper solutions in the process of purification.[1]

It was shown by Salkowski that no precipitate was formed when Fehling's reagent was added to a solution of gum arabic, but that on further addition of sodium hydroxide a precipitation was brought about. The substance precipitated was hydrolyzed with 2% sulfuric acid and formed large amounts of arabinose. On oxidation of the hydrolysate with nitric acid, there was no evidence of the formation of mucic acid. Because of these facts, Salkowski called the substance an araban.

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[1] Salkowski, *Z. physiol. Chem.*, **34**, 162 (1901); **35**, 240 (1902); **117**, 48 (1921); Henser and Braden, *J. prakt. Chem.*, **103**, 69 (1921); **104**, 259 (1922); Link, THIS JOURNAL, **51**, 2506 (1929); **52**, 2091 (1930).

Inasmuch as the original gum is known to contain galactose, the precipitation with copper would naturally seem to be a method for the concentration of the arabinose present in the gum. In fact, the procedure has been used with this end in view.[2]

Though xylans have been prepared which were largely if not wholly polymers of xylose, most of the arabans are known to form other sugars as well as arabinose on hydrolysis.[3] It is probable that the pentosan obtained from beet pectin by Ehrlich[4] is more nearly a true araban than any described previously. This substance gave 90.8% of crystalline arabinose on hydrolysis.

In order to throw further light on a rather confused subject, we have reinvestigated Salkowski's araban. It was analyzed according to methods given by Van der Haar.[5] The results obtained show that the so-called araban contains even less arabinose than arabic acid (the ash-free gum). For purposes of comparison, the analysis of the araban and of arabic acid are given in Table I.

TABLE I

ANALYSES

	Araban	Arabic acid
Pentose (as arabinose)	28.8	34.4
Methyl pentose (as rhamnose hydrate)	12.7	14.2
Hexose (galactose)	41.1	42.1
Uronic acid (glucuronic)[a]	19.5	15.5
Total	102.1	106.2

[a] That the methylpentose and aldehyde acid in gum arabic are rhamnose and glucuronic acid, respectively, was shown by the present authors [Butler and Cretcher, THIS JOURNAL, 51, 1519 (1929)].

The presence of glucuronic acid has been confirmed by Weinmann[6] and by Heidelberger and Kendall.[7]

Experimental Part

Preparation of Salkowski's Araban.—One hundred grams of gum arabic was dissolved in 2 liters of warm distilled water. To the warm solution was added one liter of Fehling's solution (made by mixing 500 cc. of solution containing 34.65 g. of copper sulfate crystals and 500 cc. of solution containing 125 g. of potassium hydroxide and 175 g. of Rochelle salt). The alkaline copper solution of gum arabic was stirred while concentrated sodium hydroxide solution (300 g. per liter) was added until no further precipitation took place. About 500 cc. of alkaline solution was required. The precipitate

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[2] For example, see Onslow, "Practical Plant Biochemistry," second edition, p. 55.

[3] Kurt Hess, "Die Chemie der Zellulose," Leipzig, **1928,** p. 46.

[4] Ehrlich and Sommerfeld, *Biochem. Z.*, **168,** 299 (1926).

[5] Van der Haar, "Anleitung zum Nachweis zur Trennung und Bestimmung der Monosaccharide und Aldehydesäuren," Berlin, **1920,** pp. 61, 71, 123.

[6] Weinmann, *Ber.*, **62,** 1637 (1929).

[7] Heidelberger and Kendall, *J. Biol. Chem.*, **84,** 639 (1929).

settled in a few minutes. The blue mother liquor was decanted and the blue precipitate was pressed between cotton cloth and filter paper. It was dissolved in 150 cc. of 1:1 hydrochloric acid and precipitated by the addition of one liter of 95% alcohol. The precipitate was allowed to settle and the alcoholic liquor was then decanted. The precipitate was washed with three successive portions of alcohol. It was redissolved in 100 cc. of water and again precipitated by alcohol. The product was washed and dried for several hours in vacuum at 70°. The samples weighed 51 g. and contained only traces of copper. $\alpha = -2.85°$ where $l = 2$ and $C = 3.94$; $(\alpha)_D$ $-36.2°$.

Anal. Subs., 0.982: CO_2 (Lefèvre method), 0.0435. Found: 4.43% CO_2, equivalent to 19.5% uronic acid. Subs., 0.491: mucic acid, 0.134. Found: galactose, 41.1. Subs., 0.491: alcohol-soluble furfural phloroglucid, 0.033; alcohol insoluble furfural phloroglucid, 0.155. From the latter figure was deducted 0.032 g. to allow for the phloroglucid due to uronic acid.[8] Found: methyl pentose (as rhamnose hydrate), 12.7; pentose (as arabinose), 28.8.

Summary

The araban of Salkowski has been shown not to be a simple polymer of arabinose but to contain arabinose, galactose, rhamnose and glucuronic acid in about the same proportion as they are present in ash-free gum arabic.

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RESEARCHES ON PYRIMIDINES. CXVIII. MOLECULAR REARRANGEMENTS IN THE THYMINE SERIES

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Hilbert and Johnson discovered that 2,6-dimethoxypyrimidine interacts with bromo-acetoglucose giving an acetyl derivative which is converted by hydrolysis into a 3-glucoside of uracil,[2] namely, "*glucuridine*." This fact was the incentive to develop the present paper, which deals with new rearrangements in the thymine series.

Thymine	I	$\mathrm{NHCONHCH{=}C(CH_3)CO}$
2,6-Dichloro-5-methylpyrimidine	II	$\mathrm{NCCl{=}NCH{=}C(CH_3)CCl}$
2,6-Dimethoxy-5-methylpyrimidine	III	$\mathrm{NC(OCH_3){=}NCH{=}C(CH_3)C(OCH_3)}$
2-Oxy-3,5-dimethyl-6-methoxy-pyrimidine	IV	$\mathrm{NCON(CH_3)CH{=}C(CH_3)C(OCH_3)}$
2,6-Dioxy-3,5-dimethylpyrimidine	V	$\mathrm{NHCON(CH_3)CH{=}C(CH_3)CO}$

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[8] Ref. 5, p. 75.

[1] Chemical Foundation Research Fellow, 1929–1930.

[2] Hilbert and Johnson, *Science*, **69**, 579 (1929); THIS JOURNAL, **52**, 200 (1930).