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## ACETYL GROUPS IN PECTIN

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In an exhaustive investigation of sugar-beet pectin by F. Ehrlich and R. v. Sommerfeld<sup>1</sup> the discovery of acetic acid as an important product of the hydrolysis of pectin is reported and it is stated that pectic acid afforded, on the average, 12.8% of acetic acid.

This, they state, occurs in the pectin in the form of acetyl groups and, by distilling the pectin solution with 1% of sulfuric acid, a mixture of acetic and formic acids passes over into the distillate. The formic acid, resulting from the decomposition of carbohydrates, is estimated by the method of Porter and Ruysen<sup>2</sup> and its equivalent in 0.1 *N* sodium hydroxide is deducted from the total titration, the difference being calculated as acetic acid.

The presence of acetyl groups has been shown in lignin and in certain forms of cellulose.

As Ehrlich and v. Sommerfeld have based their conclusion that acetic acid is a regular and important constituent of pectin substances on their investigation of beet pectin, a *root* pectin, it seemed desirable to find if acetyl groups are also present in fruit pectins.

An examination of lemon pectin, prepared in the laboratory from lemon peel by boiling for two hours with water, pressing and precipitating with alcohol, afforded only 0.37% of acid, calculated as acetic, after deducting the formic acid formed in the distillation. Apple pectin, prepared by boiling apples with water, pressing, concentrating the juice, and precipitating with alcohol, afforded the equivalent of 0.45% of acetic acid, whereas tomato pectin, prepared in the same manner, gave a little more, namely, 0.79%.

Sugar-beet pectin, prepared by boiling sugar-factory pulp for two hours with water and precipitating with alcohol, afforded 6.0% of acetic acid, determined by the method employed by Ehrlich and v. Sommerfeld.

### Experimental Part

**Lemon Pectin.**—Ten g. dissolved in 500 cc. of water with 5 g. (1%) of sulfuric acid was distilled with steam and the distillate titrated with 0.1 *N* sodium hydroxide solution, the first, second, third and fourth liters requiring, respectively, 4.7, 2.6, 1.3 and 1.1 cc. of alkali.

The total distillate was evaporated to dryness, dissolved in 200 cc. water, and 100 cc. heated on the water-bath for six hours with 5 g. of mercuric chloride and 2.75 g. of

<sup>1</sup> Ehrlich and v. Sommerfeld, *Biochem. Z.*, **168**, 263 (1926).

<sup>2</sup> Porter and Ruysen, Abderhalden's "Handbuch der biochemischen Arbeitsmethoden," Urban and Schwarzenberg, Berlin, 1910, vol. 2, p. 22.

sodium acetate. The precipitated mercurous chloride was filtered off, dried and weighed; weight, 0.0838 g. equivalent to 0.0082 g. of formic acid or 0.0164 g. in the entire distillate, which is equivalent to 3.6 cc. 0.1 *N* sodium hydroxide solution;  $9.7 - 3.6 = 6.1$  cc. of 0.1 *N* sodium hydroxide equivalent to 0.0366 g. or 0.366% of acetic acid.

**Apple Pectin.**—Eight and eighty-five hundredths g. of purified apple pectin in 500 cc. of water was treated with 30 cc. of 10% sodium hydroxide solution and let stand for 15 minutes. It was then neutralized with sulfuric acid, 5 g. in excess of sulfuric acid was added and the mixture was distilled with steam. The first, second and third liters required, respectively, 6.8, 3.4 and 1.8 cc. of 0.1 *N* sodium hydroxide solution; total, 12.0 cc.

The total distillate, when heated with mercuric chloride and sodium acetate, afforded 0.2527 g. of mercurous chloride, equivalent to 0.0246 g. of formic acid, or 5.3 cc. of 0.1 *N* sodium hydroxide solution;  $12 - 5.3 = 6.7$  cc. of 0.1 *N* sodium hydroxide solution, equivalent to 0.04 g. or 0.45% of acetic acid.

**Tomato Pectin.**—Ten g. in 500 cc. of water with 1% of sulfuric acid was distilled with steam. The first, second, third and fourth liters of distillate required 5.7, 6.0, 3.6 and 2.2 cc., respectively, of 0.1 *N* sodium hydroxide solution; total 17.5 cc.

The total distillate, treated by the Porter-Ruyssen method, afforded 0.2038 g. of mercurous chloride, equivalent to 0.0198 g. of formic acid, or 4.3 cc. of 0.1 *N* sodium hydroxide solution;  $17.5 - 4.3 = 13.2$  cc. of 0.1 *N* sodium hydroxide solution equivalent to 0.079 g. of acetic acid, or 0.79%.

**Beet Pectin.**—Ten g. in 500 cc. of water was distilled. After the first liter was distilled 1% of sulfuric acid was added and the distillation continued. The 0.1 *N* sodium hydroxide solution required was as follows: first liter, 1.85 cc.; second liter, 53.1 cc.; third liter, 33.8 cc.; fourth liter, 14.0 cc.; fifth liter, 6.5 cc.; sixth liter, 3.7 cc.; seventh liter, 2.9 cc.; eighth liter, 2.3 cc.; total, 118.15 cc.

One-half the distillate afforded 0.4268 g. of mercurous chloride or 0.8536 g. for the entire distillate, equivalent to 0.0831 g. of formic acid, or 18.07 cc. of 0.1 *N* sodium hydroxide solution;  $118.15 - 18.07$  was equivalent to 100.08 cc. of 0.1 *N* sodium hydroxide solution equivalent to 0.6006 g. or 6.0% of acetic acid. The distillate, after the removal of the formic acid, gave the odor of ethyl acetate on boiling with alcohol and sulfuric acid.

### Summary

The acetyl group, while evidently an essential constituent of beet pectin, is not an essential constituent of pectins in general.

Root pectins, such as beet pectin, may be related to or derived from lignin, ligno-cellulose or cell materials containing acetyl groups in their molecules. Fruit pectins, so far as examined, differ from sugar-beet pectin in being practically devoid of acetyl groups.

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