

48. *Alginic Acid Acetate*.

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Alginic acid and sodium and calcium alginate react at room temperature with keten to produce derivatives in which approximately one acetyl grouping is contained in each repeating unit of the chain polymers. Some properties of these acetylated materials are described.

ALGINIC acid reacts at room temperature with keten to form a colourless ester acid (I), practically insoluble in water, acetone, ethyl alcohol, methyl alcohol, ether, acetic acid, glycerol, ethyl acetoacetate, or chloroform, which can be converted into the sodium salt (II) or the calcium salt (III) by treating it with equivalent quantities of sodium or calcium hydroxide solution; these salts could also be prepared by direct reaction of keten with sodium and calcium alginate. If dried (I) is treated with sodium hydroxide, (II) is obtained in the form of a non-transparent gel, which binds about 800 mols. of water/g.-equivalent and is insoluble in acetone, ethyl alcohol, ether, acetic acid, ethyl acetoacetate, aniline, or aqueous solutions of various salts, *e.g.*, ammonium sulphate or potassium palmitate. Gels of similar properties can be prepared by bringing (I) in contact with solutions of potassium hydroxide, ammonia, trimethylamine, or guanidinium carbonate. If (I) is converted into (II) at about 60°, the salt is obtained as a transparent jelly which contains about 2500 mols. of water/g.-equivalent; this jelly can also be made by dispersing the moderately swollen form of (II) in glycerol or triethanolamine and adding water to the dispersion. A rapid de-swelling of the jelly is brought about by conversion into (I) or (III). If the glycerol dispersion of (II) is mixed with 0.1M-solutions containing calcium, magnesium, copper, or ferric ions, water-insoluble precipitates are formed.

The analyses of (I), (II), and (III) show that approximately one acetyl grouping has been introduced into each repeating unit of the chain polymers, but it is not claimed that acetyl derivatives of definite composition have been prepared. No attempt has been made to use the keten method under different conditions, *e.g.*, with catalysts, in order to obtain products of a higher acetyl content.*

The rate of alkaline hydrolysis of (II) is so great at room temperature that the direct titration of the carboxyl grouping in (I) had to be done by a special technique described below; at room temperature, on the other hand, acid hydrolysis is slow.

In order to find out whether the acetylation with keten gives rise to a marked degradation, viscosity determinations were made with solutions containing sodium alginate prepared by hydrolysis of the acetyl derivatives, taking into account the experiments of Rose (Ph. D. Thesis, London, 1937) and of Heen (*Kolloid-Z.*, 1938, **83**, 304); these tests lead to the following conclusions. During the acetylation of calcium alginate no detectable breakdown of the chain polymer appears to occur, but during the reaction with sodium alginate and with free alginic acid some degradation takes place; the viscosity of solutions containing the "recovered" sodium alginate is in all cases far higher, however, than that of solutions of low molecular uronic acids.

EXPERIMENTAL.

A 1% aqueous solution of commercial sodium alginate (η , 40 centistokes at 25°) was percolated through beds of Amberlite and Zeo-carb, and mixed with excess of N-hydrochloric acid or 0.5M-calcium acetate. The alginic acid (IV) or the calcium alginate (V) thus obtained was strained off, thoroughly washed with water, and treated with acetone until at least 95% of the gel water had been replaced. The fully acetone-swollen (IV) was suspended in acetone and mixed with an equivalent amount of N-sodium hydroxide; the sodium alginate (VI) was strained off and suspended for 24 hours in a fresh portion of dry acetone. 60 G. of fully acetone-swollen (IV) were suspended in 200 c.c. of acetone, and

* Such products have been prepared by other methods; compare Gomez, *Inst. Espan. Oceanograph., Notas y Resumenes*, Ser. II, 1933, **74**, 98; Barry, Dillon, and O'Muineachain, *Sci. Proc. Roy. Dublin Soc.*, 1933—38, **21**, 289; Cunningham, Chamberlain, and Speakman, *Nature*, 1946, **158**, 553; Carson and Maclay, *J. Amer. Chem. Soc.*, 1946, **68**, 1015.

keten was passed for 7 hours through the suspension (20°) at 0.06 g.-mol./hour. (I) was strained off, washed with acetone, water, ethyl alcohol, and ether (II and III were similarly washed), and dried at room temperature. A known quantity of (I) was suspended in water containing some phenolphthalein, and, while nitrogen was passed through the rapidly stirred mixture, successive portions of 0.3 c.c. of 0.1N-sodium hydroxide were added; after the addition of each portion the time (*t*) for disappearance of the pink colouration of the indicator was noted. In the first stage it was 1–2 minutes, but after a certain amount of alkali had been added it rose abruptly to 10–15 minutes (second stage). It is assumed that during the first stage a diffusion step and during the second stage the alkaline hydrolysis determines the value of *t*; and the alkali added during the first stage was assumed to have reacted with the free carboxyl groups. Acetyl determinations of (I), (II), or (III) were made by adding excess of 0.1N-sodium hydroxide; after 24 hours the excess was back-titrated, control determinations having shown that hydrolysis was complete [Found: C, 43.5; H, 5.2; N, < 0.2; S < 0.2; P < 0.2; carboxyl (titration), 18 ± 1 ; carboxyl (Tollens–Le Fèvre method), 19.4 ± 0.6 ; acetyl, 19 ± 1 ; acetyl + carboxyl, 36.8 ± 0.4 ; ash, 0.5. $(C_8H_{10}O_8)_x$ requires C, 41.0; H, 4.3%; carboxyl, 18.8; acetyl, 18.4; carboxyl + acetyl, 37.2%].

In estimating the approximate rate of the acid hydrolysis of (I), three portions, each containing 0.00194 g.-equiv., were placed in 10.0 c.c. of 0.1N-hydrochloric acid, the time and temperature being as follows: (1) 20 hours, 20°; (2) 93 hours, 20°; (3) 66 hours, 58°. In each run the insoluble residue obtained was filtered off and slowly washed with 1 l. of water; titration of the combined filtrate and washing showed that the hydrolysis was respectively 7.9, 20, and 100%.

0.5 G. of dried (I) was placed in water and 19 c.c. of 0.1N-sodium hydroxide were added while stirring, the gel (IIa) being filtered off after 2 hours. Fully acetone-swollen (VI) was treated with keten under conditions similar to those specified above, giving (IIb). Both samples were dried first at 20° and then at 100° to constant weight, (III) being dried in the same way [Found: (IIa): C, 35.6; H, 4.0; Na, 8.4; acetyl, 17.9. (IIb): C, 37.3; H, 3.9; Na, 8.2; acetyl, 15.0. $(C_8H_9O_8Na)_x$ requires C, 37.5; H, 3.5; Na, 9.0; acetyl, 16.8%].

0.5 G. of dried (I) and 47 c.c. of 0.04N-calcium hydroxide were mixed under conditions similar to those prevailing during the preparation of (II), giving (IIIa). Fully acetone-swollen (V), containing 0.029 g.-equiv., was placed in 350 c.c. of acetone, and keten was passed for 22 hours through the suspension (25°), at 0.02 g.-mol./hour, giving (IIIb) [Found, (IIIa) C, 37.2; H, 4.0; Ca, 7.5; acetyl, 15.4. (IIIb) C, 38.5; H, 4.5; Ca, 7.9; acetyl, 13.2. $[(C_8H_9O_8)_2Ca]_x$ requires C, 37.9; H, 3.6; Ca, 7.9; acetyl, 17.0%]. Results of typical viscosity measurements are in the accompanying Table. (I), (II), and (III) used for these tests were washed as described above but not dried.

| Alginates. | Normality of soln. with respect to | | | η (centistokes, 25°) of soln. containing | |
|------------|------------------------------------|-------------|-------|---|---------------------------------|
| | Na alginate. | Na acetate. | NaCl. | "Recovered" Na alginate. | Na alginate of control test. |
| (I) | 0.040 | 0.040 | 0.007 | 4 | 18 |
| (IIb) | 0.028 | 0.028 | 0.23 | 6 | 9 |
| (IIIb) | 0.030 | 0.030 | 0.20 | 14 | 13.8 |

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