

**102. Pectic Substances. Part II. Isolation of an Araban from the Carbohydrate Constituents of the Pea-Nut.**

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Separation of the two components of the pectic acid-araban complex present in the pea-nut was effected by lengthy extraction with aqueous alcohol. The araban so obtained was purified by converting it into the *acetate*, the properties of which are recorded. After removal of the acetyl groups, pure araban was obtained as a hygroscopic powder,  $[\alpha]_D - 160^\circ$  in water. On hydrolysis it gave quantitatively *l*-arabinose, the rate of hydrolysis indicating the presence of arabo-furanose residues in the polysaccharide. The importance of this isolation of an araban of definite purity and known properties is discussed in relation to the wide-spread occurrence of arabans in nature.

ALTHOUGH it has long been recognised that pentosans are of common occurrence in pectic materials, the difficulties encountered in attempts to effect their isolation have been so serious that no definite information has hitherto been available concerning the physical properties of these substances. This lack is felt with special force when endeavours are made to estimate the proportions of araban, galactan, and pectic acid present in the various natural pectins. The work of Ehrlich (*Biochem. Z.*, 1926, **168**, 263; 1928, **203**, 243) showed that the araban in pectins has a strong levorotation, figures ranging from  $[\alpha]_D - 25^\circ$  to  $-173^\circ$  being observed for different araban-containing preparations. For the araban which accompanies polylevans in the carbohydrate portion of Jerusalem artichokes, Schlubach and Knoop (*Annalen*, 1932, **497**, 208) have estimated a value of about  $-130^\circ$ . It is, of course, possible that various differently constituted arabans, differing in rotation, may occur in nature, and the investigation of this problem would be greatly facilitated if the arabans or their derivatives could be isolated in a condition of purity. In collaboration with Mr. G. H. Beaven we are examining the possibility of separating arabans from pectins of the citrus, apple, strawberry, raspberry and hawthorn berry types and the experimental difficulties are mainly centred in the separation of araban from its admixture with galactan. We therefore turned to another source and have succeeded in obtaining an araban in the pure state by taking advantage of the low galactan content of the pectic materials of the pea-nut (Hirst and Jones, *J.*, 1938, 502). Tedious extraction of the latter with 70% alcohol gave a solution containing araban contaminated with only small proportions of other substances. The *araban acetate* ( $[\alpha]_D - 90^\circ$  in acetone), prepared from the crude araban by treatment with pyridine and acetic anhydride, was free from galactan and pectic acid and on deacetylation it passed readily into the free araban, the rotation of which had the large negative value of  $[\alpha]_D - 160^\circ$  in water. This is close to the highest value recorded by Ehrlich and it seems likely that this preparation of Ehrlich and the material we now describe are closely similar. It will be shown in Part III (following paper) that the araban now under consideration is structurally identical with the araban present in apple pectin.

Its methyl derivative, which is obtainable with much greater ease, has already been described (Hirst and Jones, *loc. cit.*). The rotation of the methylated araban ( $-90^\circ$  in methyl alcohol) shows a marked divergence from that of the free araban, but such differences are not unusual in the arabinose series.

On hydrolysis the free araban gives crystalline *l*-arabinose in 96% yield and a comparison of the rate of hydrolysis with that of methylarabofuranoside leads to the view that the arabinose residues of the polysaccharide are exclusively furanose in type. Now  $\alpha$ -methyl-*d*-arabinoside has recently been obtained in a pure condition by Hudson and Montgomery (*J. Amer. Chem. Soc.*, 1937, 59, 992), who recorded for it  $[\alpha]_D^{20} +123^\circ$  in water. The enantiomorph in the *l*-series will therefore have the value  $-123^\circ$  and since this is close to the figure now obtained for pea-nut araban it is probable that all the glycosidic links in the polysaccharide molecule possess the  $\alpha$ -configuration.

#### EXPERIMENTAL.

*Extraction of Araban: Preparation of Araban Acetate.*—The finely powdered pectic acid-araban complex (60 g.) ( $[\alpha]_D^{20} +79^\circ$ ; equiv. wt., 452) prepared from the carbohydrate portion of the pea-nut by the method described previously (Hirst and Jones, *loc. cit.*, p. 500) was shaken at room temperature with 70% alcohol for 8 weeks. The undissolved material was then removed by filtration and the filtrate, which contained a trace of pectic acid, was neutralised with *N*/10-sodium hydroxide. On evaporation of the solution to dryness, crude araban (1.5 g.) was obtained as a brown hygroscopic solid. This was separated from sodium pectate by shaking with pyridine containing 2% of water, in which the araban dissolved. Half the volume of acetic anhydride was then added, and the solution heated at  $60^\circ$  for 12 hours. Some flocculent matter was then removed in the centrifuge and the solution was poured into water. The precipitated *araban acetate* was filtered off, washed with water until free from pyridine and acetic acid, and dried. It was a white powder (1.2 g.), soluble in acetone, hot methyl and hot ethyl alcohols (insoluble in the cold) and insoluble in light petroleum and water.  $[\alpha]_D^{20} -90^\circ$  in acetone, *c* 0.74 (Found:  $\text{CH}_3\cdot\text{CO}$ , 39.7; furfural on distillation with 12% hydrochloric acid, 31.5.  $\text{C}_9\text{H}_{12}\text{O}_8$  requires  $\text{CH}_3\cdot\text{CO}$ , 39.9; furfural, 32.0%).

*Deacetylation of Araban Acetate: Properties of Pea-nut Araban.*—The above araban acetate (0.83 g.) was deacetylated by heating for 5 hours with a slight excess of *N*-sodium hydroxide (8.0 c.c.). The solution was concentrated, and the araban precipitated by addition of alcohol. It was purified by reprecipitation from a concentrated aqueous solution by addition of alcohol, washed with alcohol, and dried in a vacuum. The free araban (0.40 g.) so obtained was a hygroscopic powder, very slightly discoloured, which dissolved readily in water. It was insoluble in acetone, ether, and alcohol, but tended to form colloidal suspensions in the last-named solvent.  $[\alpha]_D^{21} -160^\circ$  in water, *c* 1.44.

When heated with *N*/20-sulphuric acid (20 c.c.) at  $95^\circ$ , the araban (0.28 g.) was hydrolysed, the reaction being followed polarimetrically:  $[\alpha]_D^{21} -160^\circ$  (initial value, *c* 1.4);  $-94^\circ$  (35 mins.);  $-16^\circ$  (1.5 hrs.);  $+28^\circ$  (2 hrs.);  $+77^\circ$  (2.8 hrs.);  $+106^\circ$  (4.3 hrs.);  $+115^\circ$  (5.2 hrs.; constant value). On the assumption that *l*-arabinose is the only sugar formed, this final value indicates a yield of 97% of the theoretical. An aldose estimation (iodometric, by Baker and Hulton's method) gave 0.30 g. of pentose (calc., 0.318 g.). The solution was neutralised with barium carbonate and filtered. On evaporation of the solution at  $40^\circ/12$  mm., a syrup (0.30 g.) was obtained which set to a solid mass of crystalline *l*-arabinose, m. p. (without recrystallisation) and mixed m. p. with an authentic sample,  $158^\circ$ ,  $[\alpha]_D^{20} +105^\circ$  (equilibrium value in water); diphenylhydrazone, m. p.  $198^\circ$  (yield of pure *l*-arabinose, allowing for material used for rotations and titration, 96% of the theoretical).

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