Carbohydrate Research, 80 (1980) 350–353

Note

Synthesis and properties of ethyl esters of sunflower pectic acid

CHRISTO G. KRATCHANOV, MARGARITA I. KUNTCHEVA, AND NICOLAY A. KIRTCHEV
Higher Institute of Food Industries, 4000 Plovdiv (Bulgaria)
(Received August 24th, 1978; accepted for publication in revised form, September 17th, 1979)

Pectin having a very high content of polyuronic acid can be obtained easily from sunflower heads[1], so that the pectin and pectic acid are readily available for derivatisation.

Preliminary investigations of pectic acid esters with methanol, ethanol, 2-propanol, 1-butanol, ethylene glycol, and glycerol have shown that ethyl and 2-propyl pectates possess very good foaming properties. The ethyl esters have been investigated more thoroughly, since they are obtained easily and are more suitable for utilisation in the food industry.

Utilising previous data[2–4] for the production of ethyl esters of citrus pectic acid, we investigated first the esterification of sunflower pectic acid with ethanol catalysed by dry hydrogen chloride, hydrochloric acid, and sulphuric acid. All of the products (Table I) had foaming properties and were soluble in water (pectic acid is insoluble). The foaming capacity depends mainly on the degree of esterification, and the conditions of esterification had a very slight effect. The maximum foaming capacity was obtained with a degree of esterification of $>55\%$. The alcohol-soluble fraction of the ethyl pectate (Table I, sample 5b) possesses foaming properties that probably do not depend on the molecular weight of the product.

The results of the reaction of pectin with ethanol in the presence of various mineral acids are given in Table II. The foaming capacity of the mixed ethyl/methyl esters depends on the degree of esterification. The foaming properties are due to esterification of the galacturonic acid units, and sulphuric acid appears to be the most appropriate catalyst. Some of the mixed ethyl/methyl esters have a greater foaming capacity than egg albumin (*cf.* the data from Experiments 3, 6, and 8 with that for 11). The newly prepared esters are non-toxic and can therefore be used in food products.

Hydrolysis and ethanolysis of ester groups and etherification of hydroxyl groups could occur concomitantly with esterification of the carboxyl groups and trans-esterification of the methyl ester groups. Viscosity data show that extensive degradation occurs, but this has no appreciable effect on the foaming properties of the product.

TABLE I

PREPARATION OF ETHYL ESTERS OF SUNFLOWER PECTIC ACID

Sample	*Esterification conditions*			*Yield (%)*	*Degree of esterification (%)*	*Viscosity number*[5]		*Foaming capacity (%)*
	Catalyst	*Temperature (degrees)*	*Time (h)*			*Initial pectic acid*	*Ethyl pectate*	
Experiments with absolute ethanol and dry hydrogen chloride[a]								
1	1% HCl	50	240	98	36	1.2	0.50	28
2	1% HCl	65	60	83	60	1.2	0.40	92
3	2% HCl	40	240	89	50	1.2	0.41	54
4	2% HCl	50	240	90	59	1.2	0.43	90
5	2% HCl	65	60	64	68	1.2	0.32	97
5[b]	2% HCl	65	60	6	71	1.2	0.05	90
Experiments with 95% ethanol[c]								
6	2% HCl	80	16	58	41	0.88	0.30	26
7	5% HCl	80	4	75	36	0.88	0.39	20
8	10% H_2SO_4	80	4	82	33	0.43	0.22	26
9	10% H_2SO_4	60	70	87	58	0.43	0.23	94

[a]Conditions in ref. 3. [b]A fraction soluble in alcohol. [c]Conditions in ref. 4.

TABLE II

REACTION OF 95% ETHANOL WITH SUNFLOWER PECTIN

Sample	*Esterification conditions*			*Yield (%)*	*Degree of esterification (%)*	*Viscosity number*[5]	*Foaming capacity (%)*
	Acid (2M)	*Temperature (degrees)*	*Time (h)*				
Initial sunflower pectin				—	29	0.48	0
1	HCl	60	24	95	56	0.10	47
2	HNO_3	60	24	86	34	0.15	16
3	H_2SO_4	60	24	80	75	0.17	120
4	H_3PO_4	60	24	98	31	0.22	8
5	H_2SO_4	30	240	94	43	0.41	40
6	H_2SO_4	30	430	90	72	0.36	118
7	H_2SO_4	50	40	78	53	0.41	70
8	H_2SO_4	50	72	77	75	0.20	120
9	H_2SO_4	60	10	83	56	0.22	80
10	H_2SO_4	80	2	85	38	0.47	24
11	Egg albumin		—	—	—	—	100

The i.r. spectra of the supposed, mixed ethyl/methyl ester of the pectic acid (degrees of esterification 62 and 72%) contained no absorption at 930 cm^{-1} typical of the methoxy group[6], suggesting that extensive transesterification had occurred during the sulphuric acid/ethanol treatment. The absorptions at 1380 and 1410 cm^{-1} can be ascribed[6] to the deformation-stretching of the CH_3CH_2O- and -CH_2O- groups,

TABLE III

^{13}C-N.M.R. DATA FOR ETHOXY DERIVATIVES OF SUNFLOWER PECTIN

Sample	*Degree of esterification (determined by the neutralisation method)*	*Ethoxy groups (molar %)*	*Methoxy groups (molar %)*
1	56.4	87.4	12.6
2	56.6	83.8	16.2
3	63.0	92.9	7.1

respectively. These bands are absent from the spectrum of the pectin and the spectra of pectinic substances published by other authors[7-9].

The extensive occurrence of transesterification is also shown by the ^{13}C-n.m.r. data in Table III. ^{13}C-N.m.r. spectroscopy also revealed the absence of ethyl ether groups in the pectic esters.

EXPERIMENTAL

Pectic acid and pectin were obtained[10,11] from threshed sunflower heads. The moisture content of ethanol was determined interferometrically[12]. Ethanolic solutions of hydrogen chloride were obtained by using the dry gas. Other experiments involved 95% ethanol to which the appropriate amount of conc. hydrochloric acid, nitric acid, sulphuric acid, or phosphoric acid had been added.

Esterification of pectic acid or pectin was carried out as follows. A mixture of pectic acid (10 g, pectin) with ethanolic acid (100 ml) was homogenised, and stored at a given temperature. The product was collected on a G4 glass filter, washed to neutrality with 95% ethanol, and dried at 40°.

Esterifications with methanol, 2-propanol, 1-butanol, ethylene glycol, and glycerol were performed in an analogous way.

The degree of esterification of starting materials and products was determined titrimetrically[13], and the viscosity number by the method of Deuel[5]. The foaming capacity was determined by a modification of the method of Bartsch[14]. A sample (0.2 g) was homogenised with distilled water (5 ml) and then diluted to 50 ml with distilled water in a stoppered, 100-ml measuring cylinder. The solution was stirred vigorously for 1 min and the volume of foam was determined. The foaming capacity is given by 100 V_F/V_S, where V_F is the volume of foam and V_S is the volume of solution.

I.r. spectra were recorded with a Pye-Unicam SP 1000 instrument for films prepared by the method of Filippov[8]. ^{13}C-N.m.r. spectra were obtained for 3% solutions in H_2O and D_2O (4:1, internal Me_2SO) at 70° with a Varian XL-100 instrument. The chemical shifts (p.p.m. from that for Me_4Si) for the methylene and methyl groups of -CO_2 Et were δ 63.24 and 13.58, and 53.35 for MeO. Quantification was effected by comparison with the signals for carboxyl groups (δ 170.52).

REFERENCES

1 S. STOIKOFF, *Nahrung*, 3 (1958) 287–296.
2 Z. I. KERTESZ, *The Pectic Substances*, Interscience, New York, 1951.
3 R. MCDONNELL, R. JANG, E. JANSEN, AND H. LINEWEAVER, *Arch. Biochem.*, 28 (1950) 260–273.
4 M. MANABE, *Nippon Nogei Kagaku Kaishi*, 45 (1971) 417–422.
5 H. DEUEL, *Ber. Schweiz. Bot. Ges.*, 53 (1943) 219–316.
6 K. NAKANISHI, *Infrared Absorption Spectroscopy*, Holden–Day, San Francisco, 1962.
7 M. REINTJES, D. MUSKO, AND G. JOSEPH, *J. Food Sci*, 27 (1962) 441–445.
8 M. P. FILIPPOV, *Izv. Akad. Nauk Mold. SSR, Ser. Biol. Khim. Nauk*, (1970) 59–62; M. P. FILIPPOV AND T. V. VLAS'EVA, *ibid.*, (1971) 80–82.
9 M. P. FILIPPOV AND S. A. SHAMSHURINA, *Izv. Pishch. Tekhnol.*, 1 (1972) 186–190; *Chem. Abstr.*, (1972) 19912k.
10 C. KRATCHANOV, *Travaux Sci. de l'Institut Supérieur des Industries Alimentaires, Plovdiv, Bulgaria*, 13 (1966) 99–110; *Chem. Abstr.*, (1970) 44684s.
11 S. STOIKOFF AND C. KRATCHANOV, *Travaux Sci. de l'Institut Supérieur des Industries Alimentaires, Plovdiv, Bulgaria*, 13 (1966) 287–301; *Chem. Abstr.*, (1970) 65542j.
12 C. KRATCHANOV, M. I. KUNTCHEVA, AND G. IGNATOV, *Mikrochim. Acta*, (1973) 969–975.
13 H. S. OWENS, R. M. MCCREADY, A. D. SHEPHERD, T. H. SCHULTZ, E. L. PIPPEN, H. A. SWENSON, J. C. MIERS, R. F. ERLANDSEN, AND W. D. MCLAY, *Methods West. Reg. Res. Lab.*, Albany, California, AIC 340, 1952; C. L. HINTON, *Fruit Pectins*, Chemical Publishing Co., New York, 1940, pp. 27–28.
14 O. BARTSCH, *Kolloid-Beih.*, 20 (1924) 1–14.