

Raman and infrared spectra of starch samples of sweet potato and cassava

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Abstract. Raman and infrared spectra of starch samples from sweet potato and different varieties of cassava (tapioca) are reported. Three regions of the spectra, the OH stretching region ($3560\text{--}3000\text{ cm}^{-1}$), the CH stretching region ($3000\text{--}2800\text{ cm}^{-1}$) and the finger print region ($1600\text{--}200\text{ cm}^{-1}$), have been studied. The results are discussed in relation to the hydrogen bonding and the properties of starch samples.

Keywords. Vibrational spectra; starch; sweet potato; cassava; amylose; amylopectin.

1. Introduction

Raman spectra of D-glucose, cellobiose, maltose and dextran in solution in H_2O and D_2O (Spedding and Stamm 1942; Vasko *et al* 1971; Cael *et al* 1973; She *et al* 1974), of cellulose (*Valonia ventricosa*) (Blackwell *et al* 1970), of α -lactose monohydrate and β -lactose in the crystalline state and of α -lactose, β -lactose and equilibrated lactose in aqueous solution (Susi and Ard 1974) have been reported. The normal coordinate analysis of α -D-glucose (Vasko *et al* 1972; Cael *et al* 1974) and Raman spectra of crystalline α -D-glucose (Cael *et al* 1974) and D-fructose, L-sorbose and related compounds (Szarek *et al* 1984) have also been investigated. Cael *et al* (1973) have recorded and analysed the IR and Raman spectra of V_a , V_b and B-forms of potato amylose. But no such investigation has been carried out on cassava starch which is a cheap source of food, feed and industrial material. In the present work, the infrared and Raman spectra of starch samples from four different varieties of cassava namely M-4, H-165, H-1687 and H-2304 are reported and analysed, as part of a detailed investigation on the structural differences between these varieties, and are compared with the spectra of sweet potato starch.

2. Experimental

All the samples were extracted by the standard procedure (Radley 1976). Fresh tubers were freed of skin and rind and disintegrated in a waring blender at low speed. Large

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amounts of water were used. The starch milk so obtained was passed through a 260-mesh sieve to remove all fibrous impurities and allowed to settle for six hours. The supernatant water was drained off leaving the starch cake. The cake was dried in an oven at 50–60° for 6 to 8 h and then powdered.

Raman spectra were recorded on a 1401 Spex Ramalog spectrometer with a Spectra Physics model 165 argon ion laser. Spectra were recorded taking the samples as pellets and rotating these at high speeds to avoid burning of the samples. The 541.5 and 488.0 nm lines of the laser with power ranging from 80–200 mW were used. The infrared spectra were recorded using a Perkin Elmer 983 spectrophotometer. All the spectra were recorded at room temperature (300 ± 3 K).

3. Results and discussion

Three regions of the spectra have been studied: the OH stretching region, 3650–3000 cm^{-1} , the CH stretching region, 3000–2800 cm^{-1} , and the finger print region, below 1600 cm^{-1} . The observed bands for both Raman (figures 1 and 2) and IR (figure 3) spectra are given in tables 1–3.

In the OH stretching region seven bands are resolved for M-4, H-1687 and H-2304 cassava samples. The band at 3263 cm^{-1} observed in the Raman spectrum of H-165 is absent in other samples. The band near 3287 cm^{-1} found in the spectra of cassava samples is absent in the spectrum of sweet potato starch. But two additional lines appear at 3158 and 3515 cm^{-1} for sweet potato. Other lines in this region are more or less in agreement for all the samples studied. Infrared spectra of the OH stretching region of cassava and sweet potato samples show a very broad band, having a maximum at 3400 cm^{-1} .

In the general theory of sweetness (Shallenberger and Acree 1967) it is pointed out that all compounds that taste sweet belong to an AH, B system and the initial chemistry of sweet taste must therefore be concerted intramolecular hydrogen bonding between the AH, B unit of the sweet compound and a sterically commensurate AH, B unit of the receptor site. Also, a high frequency band which appears in the IR spectra of some sugar molecules has been empirically correlated to their sweetness (Shallenberger 1963; Birch 1976). The band observed at 3515 cm^{-1} in the Raman spectrum of sweet potato is significant in the reason that sweet potato is considerably sweeter than cassava. The intramolecular hydrogen bonding between the molecules of sweet potato starch and the receptor site appears to be stronger than that between the molecules of cassava starch and the receptor site.

CH stretching fundamentals are situated in a very narrow spectral region, a feature which causes an overlap of bands. M-4 and sweet potato have nine fundamental CH stretching nodes, while H-1687 and H-2304 have ten modes and H-165 has eleven. Bands around 2990 and 2911 cm^{-1} observed in the spectra of cassava samples are absent in the spectrum of sweet potato starch. In the Raman spectrum of sweet potato, an additional band appears at 2942 cm^{-1} .

Starch is a mixture of two molecular entities – a linear fraction, amylose, and its branched counterpart, amylopectin. In both the molecules, glucose in its (${}^4\text{C}_1$) form (figure 4) is the building block or repeating unit. Cassava and sweet potato starch belong to the C structure, having a lesser percentage of amylose (cassava 18% and sweet potato 20%) compared to potato starch (22%) which has a B structure (Zobel

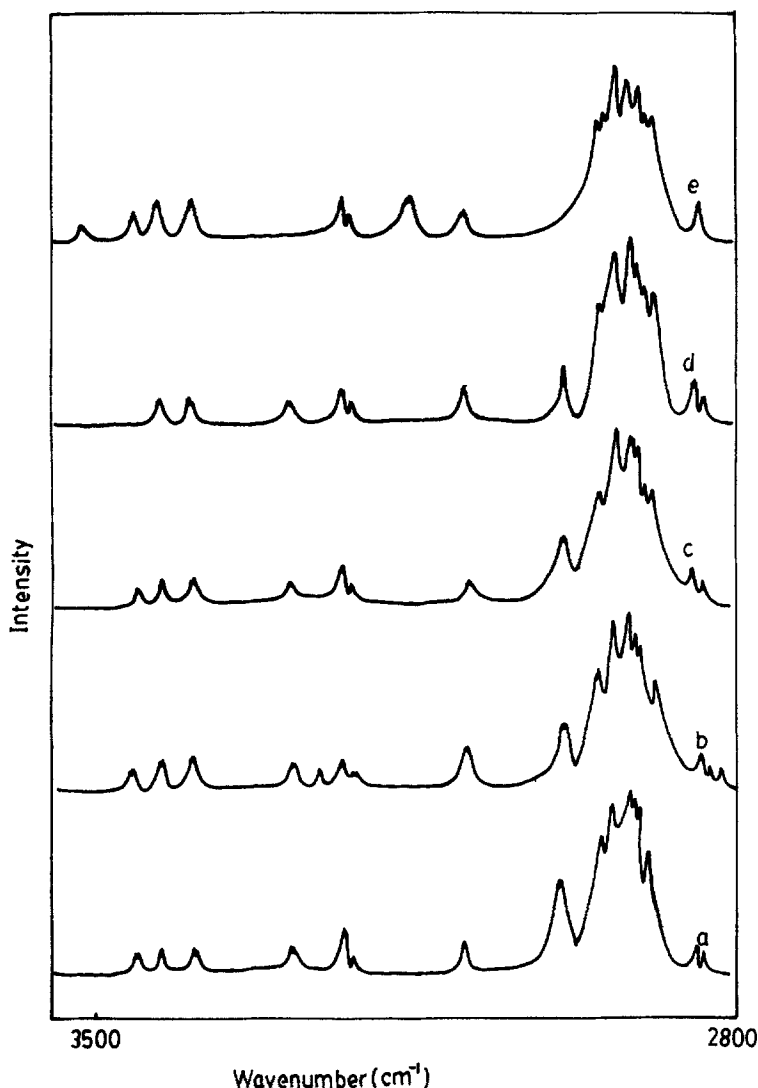


Figure 1. Raman spectra in the region $3600\text{--}2800\text{ cm}^{-1}$ of the starch samples of (a) M-4, (b) H-165, (c) H-1687, (d) H-2304 and (e) sweet potato.

1988). Amylopectin content and crystallinity are greater in cassava and sweet potato starch than in potato starch. Amylopectin exhibits an α -1, 4 backbone and a α -1, 6 branch structure with relatively short α -1, 4 branches. α -1, 6 branching that occurs with the basic building block, α -D-glucose, causes a shift in the CH stretching vibration. This leads to the absence of a 2940 cm^{-1} CH_2 stretching band, observed in the spectrum of potato amylose (Cael *et al* 1973, 1975), in the spectra of cassava samples. The 2940 cm^{-1} band is absent in the IR spectrum of the sweet potato sample. A very weak band is however observed in its Raman spectrum, probably due to the higher percentage of amylose in sweet potato starch as compared to that in cassava starch.

The observed spectra in the finger print region are similar to those of potato amylose. The CH_2 twist and C–O–H bending modes at 1334 cm^{-1} observed in potato

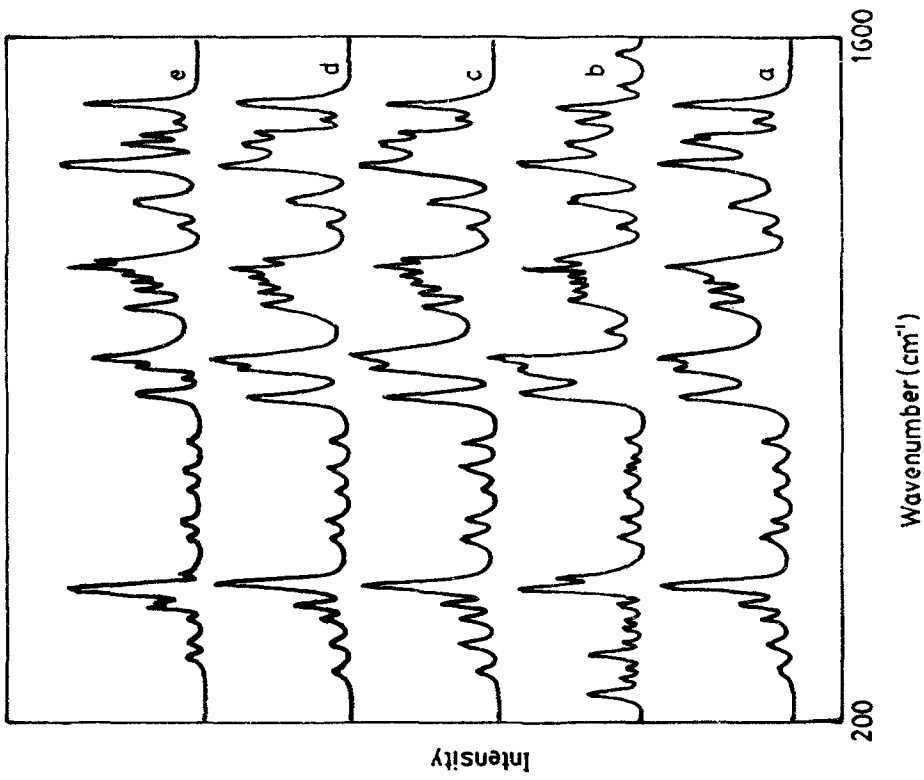


Figure 2. Raman spectra in the region $1600\text{--}200\text{ cm}^{-1}$ of the starch samples of (a) M-4, (b) H-165, (c) H-2304 and (e) sweet potato.

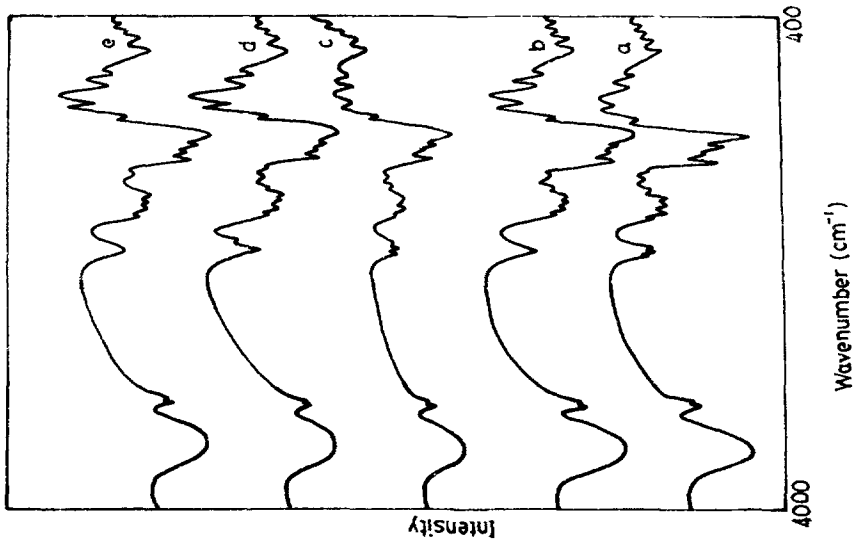


Figure 3. IR spectra in the region $4000\text{--}400\text{ cm}^{-1}$ of the starch samples of (a) M-4, (b) H-165, (c) H-2304 and (e) sweet potato.

Table 1. Raman frequencies (cm^{-1}) of starch from cassava M-4, H-165, H-1687, H-2304 and sweet potato in the region 3600–2800 cm^{-1} .

M-4	H-165	H-1687	H-2304	Sweet potato	Assignment
—	—	—	—	3515	
3455	3458	3455	3454	3460	
3431	3430	3431	3431	3434	
3393	3394	3395	3397	3397	
3286	3285	3287	3287	—	OH(stretching)
—	3263	—	—	—	
3230	3229	3229	3230	3230	
3221	3220	3222	3223	3224	
—	—	—	—	3158	
3097	3094	3093	3098	3099	
2992	2987	2990	2990	—	
2948	2951	2949	2949	2950	
—	—	—	—	2942	
2934	2933	2932	2933	2932	
2915	2917	2914	2915	2917	
2912	2910	2911	2911	—	CH(stretching)
2908	2904	2905	2905	2905	
2895	2897	2898	2899	2899	
—	2889	2891	2891	2891	
2842	—	2844	2845	2840	
2838	2837	2838	2838	2838	
—	2830	—	—	—	
—	2817	—	—	—	

Table 2. Raman frequencies (cm^{-1}) of starch from cassava M-4, H-165, H-1687, H-2304 and sweet potato in the region 1600–200 cm^{-1} .

M-4	H-165	H-1687	H-2304	Sweet potato	Assignment
—	1564	—	—	—	
—	1501	—	—	—	
1462	1454	1462	1463	1465	CH ₂ (deformation)
1429	1430	1429	1429	1429	
1401	1397	1403	1403	1402	CH(bending)
1387	1384	1385	1385	1386	
1340	1341	1342	1343	1344	CH ₂ (twist), C–O–H (bending)
1261	1272	1263	1267	1267	CH ₂ OH(related mode)
1208	1213	1212	1215	1213	
1148	1151	1147	1147	1147	C–O, C–C, C–H (related modes)
1129	1124	1130	1131	1133	
1113	1112	1115	1115	1123	
1098	1100	1098	1098	1100	
1085	1082	1085	1085	1089	C–O–H (bending)
1057	1066	1054	1054	1056	
—	997	—	—	—	
943	943	943	943	943	Skeletal mode involving α -(1 \rightarrow 4) linkage

(Continued)

Table 2. (Continued)

M-4	H-165	H-1687	H-2304	Sweet potato	Assignment
929	928	928	928	932	C–O–H (bending)
—	—	—	—	906	
870	874	866	866	873	CH and CH ₂ (deformation)
774	774	775	775	776	
—	742	—	—	—	
721	728	719	719	717	
—	714	—	—	—	
674	672	678	679	678	
610	617	621	611	611	
581	582	581	581	580	
—	501	—	—	504	
479	477	480	480	480	
—	451	—	—	450	
442	—	443	440	443	
412	412	413	412	414	
—	397	—	—	—	
360	363	363	362	364	
—	340	—	—	337	
308	313	308	305	—	
—	290	—	—	—	
—	257	—	—	—	

Table 3. Infrared frequencies (cm⁻¹) of starch from cassava M-4, H-165, H-1687, H-2304 and sweet potato.

M-4	H-165	H-1687	H-2304	Sweet potato
3400	3400	3400	3400	3400
2930	2930	2930	2930	2930
2900	2900	2890	2890	2890
1660	—	1655	—	—
1637	1638	1632	1641	1637
1600	—	—	1602	—
1455	1440	1460	1457	1452
1418	1418	1422	1415	1418
1373	1370	1373	1372	1370
1348	1345	1345	1342	1340
1315	1310	1305	1305	—
1242	1245	1245	1243	1240
1160	1160	1160	1160	1155
1105	1108	1105	1103	1100
1080	1083	1082	1083	1080
1022	1020	1025	1020	1015
935	935	932	931	930
862	862	862	862	863
765	768	770	768	770
710	710	715	715	712
580	580	580	580	580
530	530	530	530	532
480	480	480	480	480
440	440	440	440	440

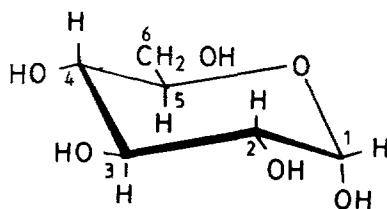


Figure 4. Structure of α -D-glucose.

amylose and α -D-glucose are observed near 1340 cm^{-1} in all the samples studied. The shift, though small, indicates α -1, 6 linkage in amylopectin in all the five samples. For D-glucose, cellobiose and maltose, Vasko *et al* (1971) assigned the band in the $1260\text{--}1280\text{ cm}^{-1}$ region to a mode involving the CH_2OH side chain. For amylose, the line at 1263 cm^{-1} is probably due to a complex mode involving the CH_2OH side chain in amylose (Cael *et al* 1973). All the samples studied showed a broad band near 1265 cm^{-1} and this could be assigned to the deformation mode of the CH_2OH side chain of the amylose present in the starch samples. The broad band indicates the presence of additional modes within the contour as in *V*-amylose.

In potato amylose, the band near 946 cm^{-1} is assigned to the skeletal mode involving α -1, 4 linkage. In the present investigation also a band is observed at 943 cm^{-1} for all the samples, as such linkages are present in both amylopectin and amylose components.

The doublet at 861 and 840 cm^{-1} corresponding to CH and CH_2 deformation modes observed in potato amylose (Cael *et al* 1975) is not found in cassava and sweet potato starch. Only one band around 870 cm^{-1} is observed in both the IR and Raman spectra of all the samples. Lack of crystalline perfection in the starch samples used for investigation, as compared to potato amylose, might have caused the decrease in the intensity of the lower band (Cael *et al* 1973).

The band near 1637 cm^{-1} in the IR spectra of the samples studied, has been attributed to the adsorbed water. This band is weaker, as the crystallinity of the sample increases. Cassava and sweet potato starch have the same crystallinity (38%). For *Valonia ventricosa*, which is recognized as the most crystalline cellulose available, this band is barely visible (Liang and Marchessault 1959). This suggests that this band arises from the vibrations of adsorbed water molecules in the non-crystalline region.

Swelling volume and swelling power are two important properties of starch. Swelling volume is the volume of the gel formed when starch is allowed to swell freely in excess water and swelling power is the weight of the starch gel obtained from undissolved starch. H-165 has the highest swelling volume and swelling power (37.8 ml/g starch, 51.8 respectively) among the four varieties of cassava investigated, H-1687 being the lowest (25.5 ml/g starch, 35.1 respectively) (Moorthy 1985). But the differences in the spectra are too obscure to reach any definite conclusion on swelling volume and swelling power.

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