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INTERPRETATION OF ^{1}H-NMR SPECTRUM OF ALGINATE BY ^{1}H-^{1}H TOCSY AND COSY SPECTRUM

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SUMMARY

The sodium alginate was prepared from brown seaweeds in Thua-Thien-Hue coastal area. The obtained alginate was characterized by ^{1}H-NMR, ^{1}H-^{1}H TOCSY and COSY spectra. The assignment of alginate peaks in ^{1}H-NMR spectrum is 5.09, 4.446, 4.152, 4.318, 4.135 ppm in correspondence to H1, H2, H3, H4, H5 of D-mannuronic acid and 5.473, 4.318, 4.446, 4.571, 4.883 ppm in correspondence to H1, H2, H3, H4, H5 of L-guluronic acid, respectively. The present results are essential for the investigating guidance of alginate and its derivatives.

I - INTRODUCTION

Alginates are quite abundant in nature since they occur both as a structural component in marine brown algae, comprising up to 40% of dry matter. All commercial alginates are at present still extracted from algal sources [1]. Alginate, a family of unbranched binary copolymers of 1-4 glycosidically linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues can be considered as patterns of homo-polymeric blocks of G and M, respectively, and blocks with an alternating sequence, all in co-existence [2]. Alginate has widespread applications in foods and drinks, pharmaceutical and bioengineering industries [3, 4]. The industrial utilization of any particular alginate will depend on its properties and therefore on its uronic acid composition, so it has become important to investigate relative proportions of the uronic acids.

The composition and sequential structure of alginate can be determined by ^{1}H-NMR and ^{13}C-NMR [4] in which the ^{1}H-NMR spectrum is very useful to quantitative analysis on the sequential structure of alginate. In the present paper, the use of ^{1}H-^{1}H TOCSY (TOtal Correlated SpectroscopY) and COSY (COrrelated SpectroscopY) spectra to interpret ^{1}H-NMR is discussed.

II - EXPERIMENTAL

Alginate was prepared from the brown seaweeds of Thua-Thien-Hue in the manner described in the preceding papers [5, 6]. The obtained alginate was characterized by ^{1}H-NMR, ^{1}H-^{1}H TOCSY, COSY using Bruker, 500 MHz. The hydrogen atoms in mannuronate and guluronate are denoted and named as G1, G2, G3, G4, G5, G6, M1, M2, M3, M4, M5 and M6 as shown in Fig. 1.

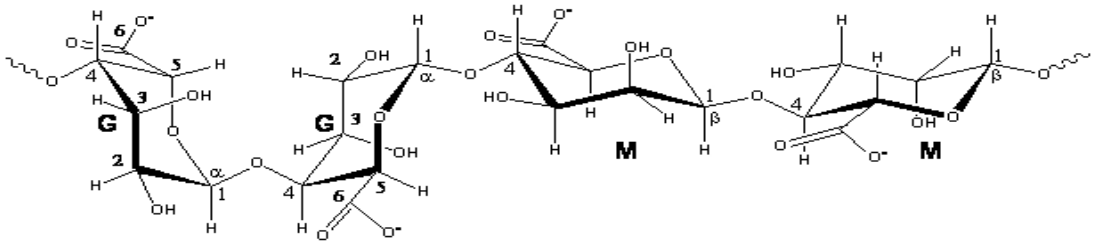

Fig. 1: Chemical block structure of alginate

III - RESULTS AND DISCUSSION

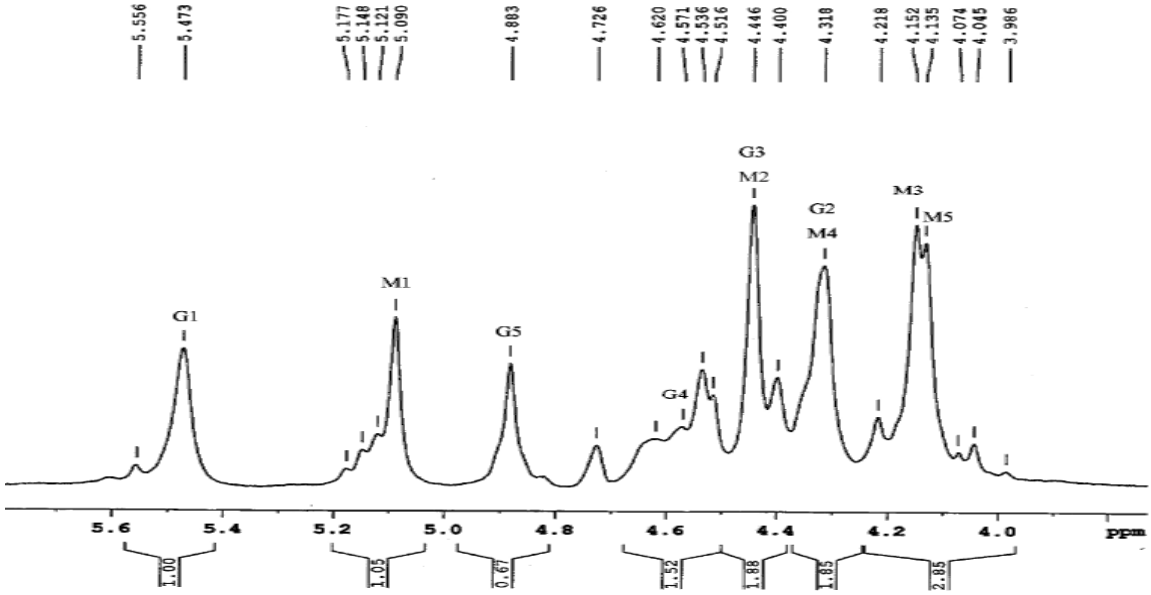

Fig. 2: [1] H-NMR spectrum of alginate

Fig. 2 shows ^{1}H-NMR of sodium alginate. ^{1}H-NMR spectrum of alginate consists of ten peaks in correspondence to 10 proton resonances of mannuronate and guluronate. Two peaks of 5.473 and 5.090 ppm located at the lowest magnetic field side should be assigned to G1 and M1, respectively because of the strongest deshielding by two oxygen atoms adjacent to them. From TOCSY spectrum as shown in Fig. 3, it can be seen that G1 interacts with the protons of G5, G4, G3, and G2 at 4.883, 4,571, 4.446, 4.318 ppm. Among of them, the peak of 4.883 ppm should be attributed to G5 due to its closer proximity to oxygen atoms of glycosidic bond. In order to interpret the neighboring proton of G1, the ^{1}H-^{1}H COSY spectrum of alginate has been recorded. Fig. 3 shows ^{1}H-^{1}H COSY spectrum of alginate. G1 only interacts with the proton at 4.318 ppm. Then the peak at 4.318 ppm should be assigned to the proton of G2. In turn, G2 interacts with the proton located at 4.446 ppm. The peak at 4.446 ppm is the resonance signal of G3. The remaining peak at 4.571 ppm is G4

peak.

In the same way, the TOCSY spectrum confirms that M1 interacts with the protons having resonance signals of 4.446, 4.318, 4.152, 4.135 ppm. From COSY spectrum, the peak at 4.446 ppm resulted in interaction of M1 should be attributed to the proton of M2. Referring back to TOCSY spectrum, in addition to the interaction with M2, M1 interacts with two protons at 4.152 and 4.318 ppm. Two these peaks belong to M3 and M4. On the other hand, the interaction of M1 with the proton at 4.152 ppm is observed in COSY spectrum. As a result, the resonance signal at 4.152 ppm should be assigned to M3. The remaining peak at 4.318 ppm is assigned to M4. The resultant assignment of alginate peak is listed on table 1. and Fig. 2.

Table 1: Chemical shift of protons of D-mannuronic acid (M) and L-guluronic acid (G).

Acid	H1	H2	H3	H4	H5
D-mannuronic acid (M)	5.090	4.446	4.152	4.318	4.135
L-guluronic acid (G)	5.473	4.318	4.446	4.571	4.883

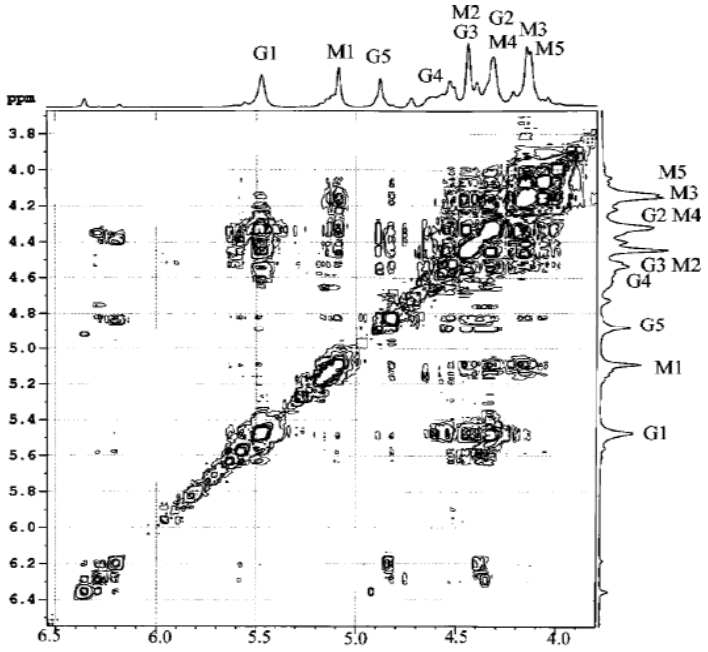

Fig. 3: ^{1}H-^{1}H TOCSY spectrum of alginate

IV - CONCLUSION

The ^{1}H-MNR spectrum of alginate was interpreted by ^{1}H-^{1}H TOCSY and COSY spectra. Using both ^{1}H-^{1}HTOCSY and COSY spectrum allows gaining insight the structure of alginate. The present results are essential for the investigating guidance of alginate and its derivatives.

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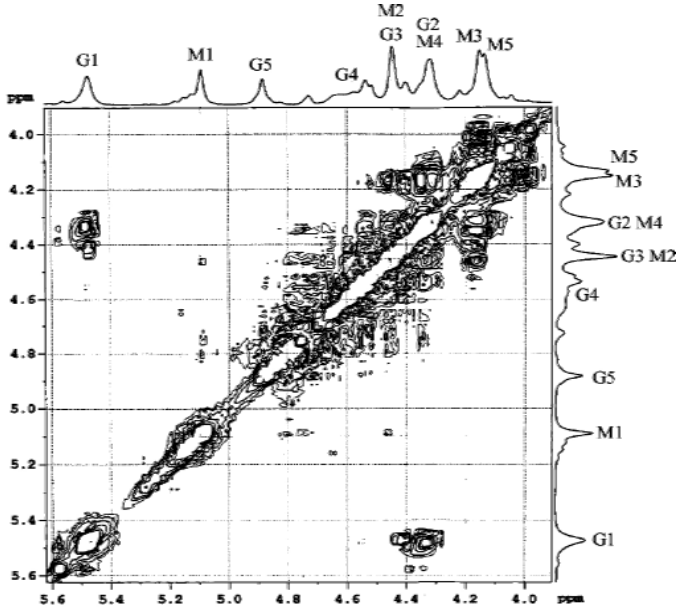

Fig. 4: COSY spectrum of alginate