

# 含硫率對磺酸幾丁聚醣與磺酸苯幾丁聚醣抑菌作用及水溶性之影響

蘇俊旗、陳齊聖

E-mail: 9015666@mail.dyu.edu.tw

## 摘要

利用來自蝦殼的幾丁聚醣產品，以化學法製造出不同去乙醯度（DD）的幾丁聚醣，分別在 PYRIDINE 及 METHANOL 相中，進行化學修飾，得磺酸幾丁聚醣（SC）和磺酸苯幾丁聚醣（SBC）。本研究選擇不同含硫率（1~5%）及不同去乙醯度的 SC 及 SBC 對 ESCHERICHIA COLI (CCRC 10674)、SALMONELLA TYPHIMURIUM (CCRC 10746) 及 STAPHYLOCOCCUS AUREUS (CCRC 12652) 做最低抑菌濃度（MIC）的測試，更進一步探討含硫率對 SC 及 SBC 水溶性之影響。研究結果顯示，溶解度隨著含硫率的增加而增加，然而含硫率的增加並不會有較好的抑菌效果，另一方面，不同的菌株對含硫率的敏感度不一，所以各種菌株對含硫率的要求也不盡相同。而去乙醯度也會影響 SC 及 SBC 的性質。SC 及 SBC 均比幾丁聚醣有較顯著的抑菌效果，且 SBC 富水溶之特性，可增加未來應用之潛力。

關鍵詞：去乙醯度、含硫率、幾丁聚醣、磺酸幾丁聚醣、磺酸苯幾丁聚醣、最低抑菌濃度

## 目錄

1.前言--P1  
2.文獻回顧--P4  
2.1 幾丁質與幾丁聚醣的發現與分佈--P4  
2.2 幾丁質與幾丁聚醣的構造--P4  
2.3 幾丁質與幾丁聚醣結構間之相關性--P5  
2.4 幾丁質與幾丁聚醣之理化特性--P6  
2.4.1 溶解性與黏度--P6  
2.4.2 與金屬離子錯合--P6  
2.4.3 剪力--P7  
2.4.4 熱裂解--P7  
2.4.5 吸附能力--P7  
2.5 幾丁質與幾丁聚醣之製備--P8  
2.5.1 幾丁質之製備--P8  
2.5.2 幾丁聚糖之製備--P9  
2.6 幾丁聚醣去乙醯程度的測定--P9  
2.6.1 膠體滴定法--P9  
2.6.2 酸鹼滴定法--P10  
2.6.3 中性滴定法--P10  
2.6.4 紅外線光譜分析法--P11  
2.7 幾丁聚醣分子量之測定--P12  
2.7.1 黏度平均分子量法--P12  
2.8 幾丁質與幾丁聚醣之化學修飾--P13  
2.9 幾丁聚醣之抑菌機制--P13  
2.10 幾丁質與幾丁聚醣之應用--P14  
2.10.1 廢水處理--P14  
2.10.1.1 凝聚劑--P14  
2.10.1.2 吸附重金屬--P14  
2.10.1.3 去除放射性元素--P14  
2.10.1.4 吸附反應性染料--P15  
2.10.1.5 污水處理場之污泥脫水--P15  
2.10.2 醫藥方面--P15  
2.10.3 食品方面--P15  
2.10.4 農業方面--P16  
3.材料設備與方法--P17  
3.1 實驗材料--P17  
3.1.1 食品原料--P17  
3.1.2 幾丁聚醣--P17  
3.1.3 化學藥品--P17  
3.1.4 培養基--P17  
3.1.5 實驗菌株--P17  
3.2 設備--P18  
3.3 實驗方法--P18  
3.3.1 SULFONATED CHITOSAN 之製備--P18  
3.3.2 不同含硫率磺酸幾丁聚醣之製備--P19  
3.3.3 SULFOBENZOYL CHITOSAN 之製備--P19  
3.3.4 不同含硫率磺酸苯幾丁聚醣之製備--P19  
3.3.5 不同去乙醯度之幾丁聚醣之製備--P19  
3.3.6 幾丁聚醣去乙醯程度的測定--P19  
3.3.7 幾丁聚醣分子量的測定--P20  
3.3.8 溶解度測定--P20  
3.3.9 抑菌測試--P20  
3.3.10 元素分析--P21  
4.結果於討論--P23  
4.1 鹼液濃度及反應時間對幾丁質去乙醯效果之影響--P23  
4.2 幾丁聚醣及其衍生物之抑菌能力--P24  
4.2.1 磺酸幾丁聚醣之抑菌效果--P24  
4.2.2 磺酸苯幾丁聚醣之抑菌效果--P25  
4.2.3 去乙醯度對磺酸苯幾丁聚醣之抑菌效果--P26  
4.3 幾丁聚醣及其衍生物之水溶性--P27  
4.3.1 磺酸幾丁聚醣的水溶性--P27  
4.3.2 磺酸苯幾丁聚醣的水溶性--P27  
4.3.3 去乙醯度對磺酸苯幾丁聚醣之溶解度--P28  
4.4 含硫率與去乙醯度之交互作用--P29  
5.結論--P31

## 參考文獻

1. 山口壽，1986，幾丁質與幾丁聚醣在食品與醫藥上之應用，食品開發，21 (8) :20-23。 ( JAPANESE )
2. 方紹威，1989，幾丁聚醣的抑制微生物作用及其在低糖金橘蜜餞之應用，國立台灣大學食品科技研究所碩士論文。
3. 王綺芬，1989，蟹殼幾丁質產品理化性質測定及製備方法之研究，國立台灣大學食品科技研究所碩士論文。
4. 王三郎，1996，水產資源利用學，高立圖書有限公司，台北。
5. 李勳宜，1988，草蝦幾丁聚醣之製備及其應用研究，國立台灣大學食品科技研究所碩士論文。
6. 林孫基、劉仁煥，1994，以生物性高分子-幾丁質 (CHITIN) 衍生物處理危害性有機污染廢液之研究，樹德學報，15: 147-193。
7. 林瑞洵、蔣蘇洪、張慕珊，1992，脫乙醯度測定方法，化學通報，3: 39-42。
8. 陳懿慧、李錦楓，1996，幾丁聚醣應用於葡萄柚汁澄清之探討，食品科學，23 (5) :617-628
9. 張鈺驥，1987，草頭蝦中幾丁質類產品的製備方法、理化性質與應用，國立台灣大學農業化學研究所碩士論文。
10. 蔡敏郎，1993，不同分子量、不同去乙醯度的幾丁聚醣溶液的流變性質與膠囊物性的關係，國立台灣海洋大學水產食品科學研究所碩士論文。
11. 蔡正芳，1992，不同去乙醯的幾丁聚醣對微生物的作用及澀味的影響，國立台灣大學食品科技研究所碩士論文。
12. 廖萬裕，1997，幾丁聚醣及其衍生物之抑菌研究，私立大葉工學院食品工程研究所碩士論文。
13. 劉瓊淑，1994，幾丁質，幾丁聚醣及相關酵素之特性與應用，食品工業，26 (11) : 26-36。
14. 錢明賽，1977，水產廢棄物蝦、蟹外殼利用之研究，食品工業發展研究所報告 118 號。
15. 錢明賽、賴淑琪，1979，CHITOSAN 在廢水處理上之應用，食品工業發展研究所報告 151 號。
16. AUSTIN, P. R., BRINE, C. J., CASTLE, J. E., AND ZIKAKIS, J. P. 1981. CHITIN: NEW FACETS OF RESEARCH. SCIENCE. 212: 749-753.
17. BIHARI-VARGA, M., SEPULCHRE, C., AND MOCZAR, E. 1975. THERMOANALYTICAL STUDIES ON PROTEIN-POLY-SACCHARIDE COMPLEX OF CONNECTIVE

TISSUE. J. THERMAL ANAL. 7 : 675. 18. BAXTER, A., DILLON, M., TAYLOR, K. D. A., AND ROBERTS, G. A. F. 1992. IMPROVED MET -HOD FOR I.R. DETERMINATION OF THE DEGREE OF N-ACETYLATION OF CHITOSAN. INT. J. BIOL. MACROOMOL., 14: 166-169. 19. BOUGH, W. A. AND SALTER, W. L. 1978. INFLUENCE OF MANU FACTURING VARIABLES ON THE CHARACTERISTICS AND EFFECTIVENESS OF CHITOSAN PRODUCTS. I. CHEMICAL COMPOSITION, VISCOCITY, AND MOLECULAR - WEIGHT DISTRIBUTION OF CHITOSAN PRODUCTS, BIOTECH. BIO -ENG. 20 : 1931. 20. CHEN C. S. AND LIAU W. Y. AND TSAI G. J. 1998. ANTIBACTERIAL EFFECTS OF N-SULFONA -TED AND N-SULFOBENZOYL CHITOSAN AND APPLICATION TO OYSTER PRESERVATION. FOOD PROT -ECTION., JOURNAL,61(9):1124-1128. 21. DOMSZY, J. G. AND ROBERTS, G. A. F. 1985. EVALUATION OF INFRAREED SPECTROSCOPIC TECHNIQES FOR ANALYSING CHITOSAN. MAKROMOL. CHEM. 186: 1671-1677. 22. GHIAUTH, A E., ARUL, J., GRENIER, J., AND ASSELIN, A. 1992. ANTIFUNGAL ACTIVITY OF CHITOSAN ON TWO POSTHARVEST PATHOGENS OF STRAWBERRY FRUIT.PHYTOPATHOLOGY.82:398-402. 23. HADWIGER, L. A. AND BECKMAN, J. M. 1980. CHITOSAN AS A COMPONENT OF PEA-FUSARIUM AOLANI INTERACTION. PLANT PHYSIOL.66:205-211. 24. HADWIGER, L. A. AND BECKMAN AND ADAMS, M. J. 1981. LOCALIZATION OF FUNGAL COMPONE -NTS IN THE PEA-FUSARIUM INTERACTION DETECTED IMMUNOCHEMICALLY WITH ANTI-CHITOSAN AND ANTI-FUNGAL CELL ANTISERA. PLANT PHYSIOL. 67:170-175. 25. HADWIGER, L. A. AND LIN, R. F. 1982. HEXOAMINE ACCUMULATIONS ARE ASSOCIATED WITH THE TERMINATED GROWTH OF PUCCINIA STRIIFORMIS ON WHEAT ISOLINES. PHYSIOL. PLANT. PATHOL. 19:249-255. 26. HADWIGER, L. A., KENDRA, D. F., FRISTENSKY, B. W. AND WAGONER, W. 1986. CHITOSAN BOTH ACTIVATES GENES IN PLANTS AND INHIBITS RNA SYNTHESIS IN FUNGI. IN "CHITIN IN NATURE AND TECHNOLOGY",PP.209-214, MUZZARELLI,R.JEUNIARX,C. AND GOODAY,G.(ED.) , PLENUM PRESS, N.Y. 27. HIRANO, S., OHE, Y., AND ONE, H. 1976. SELECTIVE N-ACYLATION OF CHITOSAN. CARBOHY -DR. RES. 47: 315-320. 28. HIRANO, S. 1988. PRODUCTTION AND APPLICATION OF CHITIN AND CHITOSAN IN JAPAN. IN PROCEEDING OF THE FOURTH INTERNATIONAL CONFERENCE ON CHITIN AND CHITOSAN, PP.37-43 , SKJAK-BRAEK, G. ANTHONSEN, T. AND SANDFORD, P. ( ED.) , ELSEVIER APPLIED SCI. PUBLISHERS, LONDON. 29. HIRANO, S., KINUGAWA, J., AND NISHIOKA, A. 1989. SULFATED DERIVATIVES OF CHITOSAN AND THEIR CHARACTERIZATION WITH RESPECT TO BIOLOGICAL ACTIVITY. IN CHITIN IN NATURE AND TECHNOLOGY, PP. 461-467, MUZZARELLI, R., JEUNIARX, C. AND GOODAY, G. ( ED. ) , PLENUM PRESS, N.Y. 30. KENDRA D. F. AND HADWIGER, L. A. 1984. CHARACTERIZATION OF THE SMALLEST CHITOSAN OLIGOMER THAT IS MAXIMALLY ANTIFUNGAL TO FUSARIUM SOLANI AND ELICITS PISATIN FORMA -TION IN PISUM SATIVUM. EXP. MYCOL. 8:276-281. 31. KNORR, D. 1984. USE OF CHITINOUS POLYMERS IN FOOD-A CHALLENGE FOR FOOD RESEARCH AND DEVELOPMENT. FOOD TECHNOL., JOURNAL: 85-97. 32. KNORR, D. 1991 RECOVERY AND UTILIZATION OF CHITIN AND CHITOSAN IN FOOD PROCESSING WASTE MANAGEMENT. FOOD TECHNOL., JOURNAL: 114-122. 33. KNORR, D. 1986. NUTRITIONAL QUALITY, FOOD PROCESSING, AND BIOTECHNOLOGY ASPECTS OF CHITIN AND CHITOSAN: A REVIEW. PROCESS BIOCHEMISTRY., 21 ( 3 ) : 90-92. 34. KURITA, K. 1986. CHEMICAL MODIFICATIONS OF CHITIN AND CHITOSAN. IN "CHITIN IN NATU -RE AND TECHONOLOGY",PP.287-293, MUZZARELLI, R.,JEUNIAUX,C.AND GOODY,G.W.(ED),PLEN -UM PRESS, N.Y. 35. LANG, G AND WELLA, T. C. 1989. THE USE OF CHITOSAN IN COSMETICS. IN "CHITN AND CHIT -OSAN",PP.139-147, SKJAK-BRAEK, G., ANTHOSEN, T. AND SANFORD, P.( ED )ELSEVIER APPLIED SCIENCE, N.Y. 36. LEUBA, J. L., AND P. STOSSEL. 1986. CHITOSAN AND OTHER POLYAMINES:ANTIFUNGAL ACTIV -ITY AND INTERACTION WITH BIOLOGICAL MEMBRANES, P.215-221. IN R. MUZZARELLI, C. JEUNIARX, AND G. GOODAY(ED), CHITIN IN NATURE AND TECHNOLOGY. PLENUM PRESS. NEW YORK. 37. MIMA, S., MIYA, M., IWAMOTO, R., AND YOSHIKAWA, S. 1982. HIGHLY DEACETYLATED CHITO -SAN AND ITS PROPERTIES. PROC. SECOND INTERNATIONAL CONFERENCE ON CHITIN/CHITOSAN, P.21. 38. MIMA, S., MIYA, M., IWAMOTO, R., AND YOSHIKAWA, S. 1983. HIGHLY DEACETYLATED CHITO -SAN AND ITS PROPERTIES. J. APPL. POLYMER SCI., 28: 1909-1917. 39. MOORE, G. K. AND ROBERTS, G. A. F. 1980. DETERMINATION OF THE DEGREE OF N-ACETYLA -TION OF CHITOSAN . INT. J. BIOL. MACROMOL., 2, APRIL: 115-116. 40. MUZZARELLI, R. A. A. 1997 OXFORD. O'BRINE, M. AND COLWELL, R. R. CHITIN. PREGAMON PRESS. A RAPID TEST FOR CHITINASE ACTIVITY THAT USES 4-METHYLUMBELLIFERYL-N-ACETYL - -D-GLUCOSAMINE. APPL. AND ENVIR. MICROB., 53 : 1718-1724. 41. MUZZARELLI, R. A. A., TANFANI, F., EMANUELL, M., CHIURAZZI, E. AND PIANI, M. 1986 . SULFATED N-CARBOXYMETHYL CHITOSANS AN BLOOD ANTICOAGULANTS. CHITIN IN NATURE AND TECHONOLOGY , PP.469-467, MUZZARELLI, R., JEUNIAUX, C. AND GOODY, G. W. ( ED ), PLENUM PRESS, N.Y. 42. NIL. 1996. MARKET OF CHITIN AND CHITOSAN. BIO INDUSTRY, 13 ( 3 ) :52-61. ( JAPANESE ) 43. NISHIMURA, K., NISHIMURA, S., NISHI, N., SAIKI, I., TOKURA, S. AND AZUMA, I. 1984. IMMUNOLOGICAL ACTIVITY OF CHITIN AND ITS DERIVATIVES. VACCINE 2 : 93-99. 44. NISHI, N., NOGUCHI, J., TOCURA, S., AND SHIOTA, H. 1979. STUDIES ON CHITIN I.ACETY -LATION OF CHITIN. POLYMER JOURNAL.11 ( 1 ) :27-32. 45. OKIEI, W., NISHIMURA, S., SOMORIN, O., NISHI, N. AND TOKURA, S. 1986. INHIBITORY ACTION OF SULFATED CHITIN DERIVATIVES ON THE HYDROLYTIC ACTIVITY OF THROMBIN. IN" CHITIN IN NATURE AND TECHOLOGY ", PP.433-460, MUZZARELLI,R.JEUNIAUX,C.AND GOODY, G. W. ( ED ), PLENUM PRESS, N.Y. 46. PEARCE, R. B. AND RIDE, J. P. 1982. CHITIN AND RELATED COMPOUNDS AS ELICTORS OF THE LIGNIFICATION RESPONSE IN WOUNDED

WHEAT LEAVES. PHYSIOL.PLANT PATHOL.20:119-129. 47. POUICEK, M., VOSS-FOUCART, M. F., AND JEUNIAUX, C. 1986. CHITINPROTEIC COMPLEXES AND MINERALIZATION IN MOLLUSK SKELETAL STRUCTURES. IN PROCEEDINGS OF THE THIRD INT -ERNATIONAL CONFERENCE ON CHITIN AND CHITOSAN, PP.7-12. PLENUM PRESS, N.Y. 48. RICO-MUNOZ, E., AND P. M. DAVIDSON. 1983. EFFECT OF CORN OIL AND CASEIN ON THE AN -TIMICROBIAL ACTIVITY OF PHENOLIC ANTIOXIDANTS. J. FOOD SCI. 48:1284-1288. 49. ROBERTS, G. A. F. 1992. CHITIN CHEMISTRY. THE MACMILLAN PRESS LTD, LONDON. 50. ROBERTS, G. A. F. AND DOMSZY, J. G. 1982. DETERMINATION OF THE VISCOMETRIC CONSTAN -TS FOR CHITOSAN. INT. BIOL. MACROMOL., 4: 374-377. 51. STANLEY, W.L., WATTERS, G.G., CHAN, B.G., CHAN, B.G., AND MERCER, J.M. 1975. LACTO- -SE AND OTHER ENZYMES BOUND TO CHITIN WITH GLUTARALDEHYDE. BIOTECH. AND BIOENG., XVII: 315-326. 52. SUDARSHAN, N. R., D. G. HOOVER, AND D. KNORR. 1992. ANTIBACTERIAL ACTION OF CHITOS -AN. FOOD BIOTECHNOL. 6(3):257-272. 53. TOEI, K. AND KOHORA, T. 1976. A CONDUCTOMETRIC METHOD FOR COLLOID TITRATIONS. ANAL -YTICA CHIMICA ACTA. 83: 59-65. 54. URAGAMI, T. 1992. SEPARATION OF ORGANIC LIQUID MIXTURES THROUGH CHITOSAN AND CHITO -SAN DERIVATIVE MEMBRANES BY PERVAPORATION AND EVAPOMEATION METHODS. IN "ADVANCES IN CHITIN AND CHITOSAN".PP.594-603, BRINE, C. J., SANDFORD, P. A. AND ZIKAKIS, J. P. ( ED ), ELSEVIER APPLIED SCIENCE. N.Y. 55. WOLFROM, M. L. JOHNSON, AND H. T. M. SHEN. 1959. THE SULFONATION OF CHITOSAN. J. AM. CHEM. SOC. 81:1764-1766.