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Research Article

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The Structure Elucidation of a Component in Essential Oil of *Citrus Reticulata* Blanco Peel by its Mass Spectrum

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ABSTRACT

A peak including an unknown component in the total ion chromatogram of essential oil from Citrus reticulata Blanco peel, which retention index is nearly the same as that of tetradecanoic acid (1748) in apolar column, can't match a suitable compound through the searching of NIST08 (National institute of science and technology) MS (mass spectrum) database. Its' structure was tentatively elucidated by the mass spectrum. In the end, the most probably identity was deduced, and its correction will be confirmed in the following research.

Keywords: Structure elucidation; Essential oil; *Citrus reticulata* blanco; Mass spectrum

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INTRODUCTION

In previous studies, the essential oils of peels from many varieties of *Citrus* reticulata Blanco in China, such as *C. reticulata* 'Dahongpao', *C. reticulata* 'Ponkan', *C. kinokuni* Tanaka, and etc., was extracted by hydro distillation.

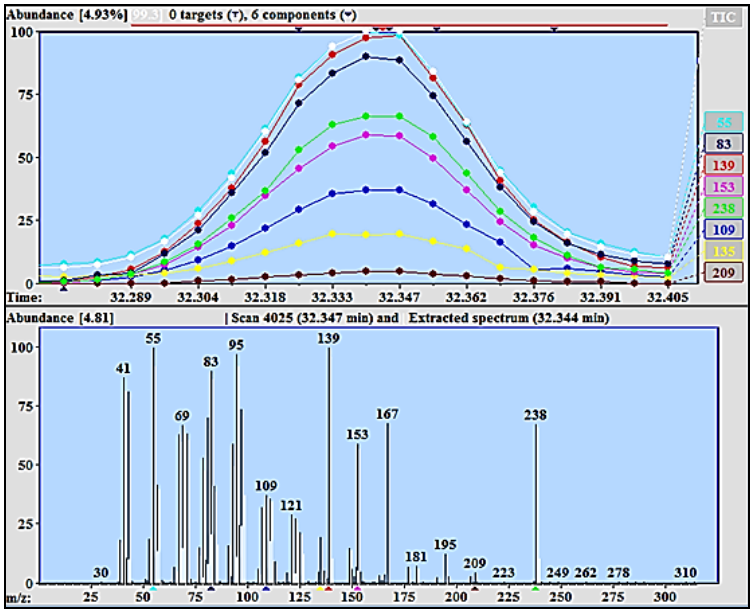

Figure 1: Purity of the peak with retention time (RT) as 32.35 min from TIC of essential oil of *C. reticulata* 'Ponkan' peel collected from Sichuan province; China in December, 2011 was detected by AMDIS

The total ion chromatograms (TICs) of these oils were obtained by gas chromatography-mass spectrometer

(GC-MS). In the course of component identification, a peak existed in some TICs which retention index (RI) is nearly the same as that of tetradecanoic acid (1748, provided by National institute of science and technology (NIST) 08 MS (mass spectrum) database), was corresponding to a chemical using the detection of Automated Mass spectrum Deconvolution and Identification System (AMDIS), which was displayed in Figure 1.

MATERIALS AND METHODS

The corresponding components provided by NIST search and probability based matching (PBM) couldn't match the chemical of the peak through the detailed comparison of their MS and RI. In such conditions, the author decided to elucidate the component's structure by its mass spectrum. The detailed information of its ion peaks extracted from the mass spectrum is shown in Table 1.

Table 1: The detailed information of ion peaks. The value in bracket is the relative intensity of corresponding ion peak (maximum value is 100)

Characteristic peak	Vicinity peaks	The ion pairs to form molecular weight (M_W)	The ion pairs that interval between 2 or 4
55 (100)	57 (39) 53 (18) **56** (14) **54** (12) 51 (2.4) 52 (1.6) 58 (2.3) 59 (1.7)	**56** (14) 182 (1.5), 57 (39) **181** (7.6), 59 (1.7) 179 (0.7); **139** (96) 99 (10), 140 (11) **98** (35), 141 (2.2) 97 (71), **138** (2.6) 100 (0.8), **135** (21) 103 (0.5); **83** (91) 155 (1.3), **84** (38) 154 (9.5), 85 (16) **153** (60), 86 (1.6) **152 (7.0),** 87 (0.6) 151 (3.5); **43 (83) 195** (13), **42 (10)** 196 (3.6); **167** (68) 71 (63), 168 (8.8) **70** (24), 169 (1.0) **69** (66), 165 (2.0) 73 (1.1), **166** (3.4) 72 (3.6); **109** (38) 129 (0.9), 111 (37) 127 (3.4), **110** (20) 128 (0.9), 113 (10) 125 (22), 114 (1.0) 124 (5.1).	**209** (4.5) 207 (3.0)**, 195** (13) **191** (2.7), **181** (7.6) 179 (0.7) **177** (7.1), **167** (68) 165 (2.0) **163** (3.5), **153** (60) 151 (3.5) **149** (15), **139** (96) 137 (6.2) **135** (21), 125 (22) 123 (26) **121** (30), 111 (37) **109** (38) 107 (29), 97 (71) **95** (95) 93 (53), **83** (91) 81 (68) 79 (50), **69** (66) 67 (64) 65 (8.0), **55** (100) 53 (18) 51 (2.4), **41 (86) 39 (18)**
139 (96)	140 (11) 141 (2.2) 137 (6.2) **138** (2.6) **136** (4.4) **135** (21)		
95 (95)	97 (71) 93 (53) **98 (35)** 96 (26) 91 (16) 94 (12) 99 (10) 92 (3.0) 100 (0.8) 103 (0.5)		
83 (91)	81 (68) 79 (50) **84** (38) **82** (21) 85 (16) 77 (12) 80 (8.0) 78 (3.9) 86 (1.6) 87 (0.6)		
41 (86)	**43 (83) 39 (18) 42 (10)**		
167 (68)	168 (8.8) 169 (1.0) **163** (3.5) 164 (1.4) 165 (2.0) **166** (3.4)		
69 (66)	67 (64) 71 (63) **70** (24) **68** (15) 65 (8.0) 66 (6.5) 72 (3.6) 73 (1.1)		
238 (66)	239 (11) 240 (1.0) 237 (0.9)		
153 (60)	154 (9.5) 155 (1.3) **152 (7.0)** 151 (3.5) **150 (6.6) 149** (15)		
109 (38)	111 (37) 107 (29) **110** (20) 113 (10) **108** (8.0) 105 (4.9) 114 (1.0)		
121 (30)	123 (26) 125 (22) **126** (15) 122 (5.1) 124 (5.1) 127 (3.4) 128 (0.9) 129 (0.9) 119 (1.1) 120 (0.7)		
195 (13)	196 (3.6) **191** (2.7) 192 (0.8)		
209 (4.5)	207 (3.0) 208 (0.9) 210 (1.0)		
181 (7.6)	**177** (7.1) 178 (1.7) 179 (0.7) 182 (1.5)		
223 (0.8)	220 (0.7)		

The chemical's M_W should be 238, and the compound should belong to sesquiterpenoid, and as such, its formula would be $C_{15}H_{26}O_2$, which unsaturated index is 3. The most probably matched compound using the NIST search was widdrol hydroxyether (its structure can be seen in Figure 2); the comparison of their mass spectra could be seen in Figure 3.

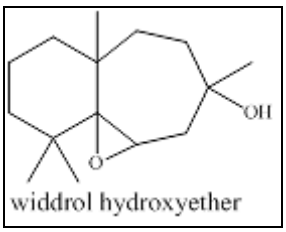

Figure 2: The structure of widdrol hydroxyether

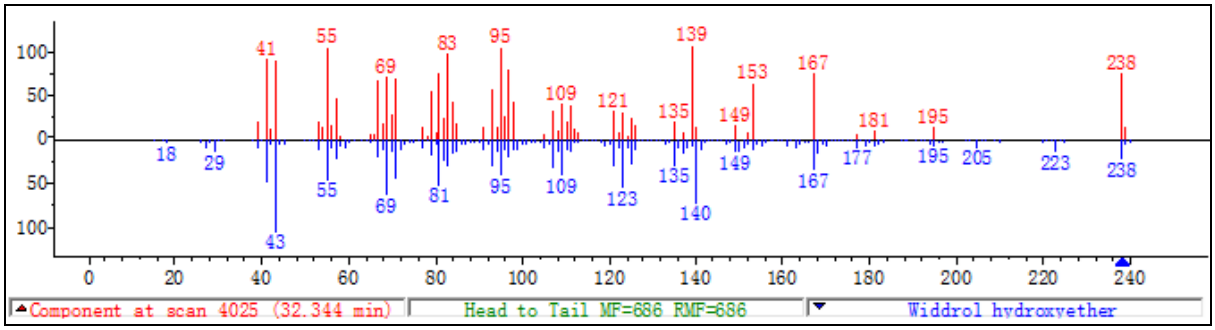

Figure 3: The comparison of mass spectra of unknown component and widdrol hydroxyether

RESULTS AND DISCUSSION

Such information gave some hints that the structure maybe similarity with widdrol hydroxyether. The ion peak 139 (96) should be an important hint to elucidate the structure. The ion peak 139, which abundance is nearly as a base peak, demonstrated that the compound most probably belongs to carotanoid, which is formed through the way listed below (Figure 4).

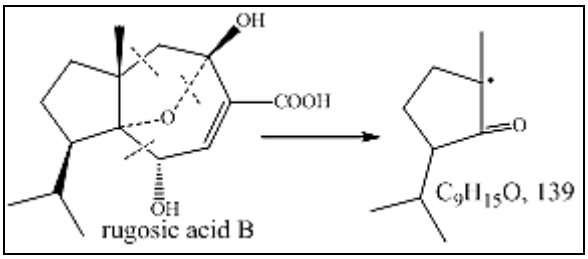

Figure 4: The ionization pathway of base peak as m/z 139 of rugosic acid B

The ion peak m/z 139 is the base peak of rugosic acid B, which belongs to carotenoid [1,2]. By now, the compound's main structure can be elucidated as the following (Figure 5).

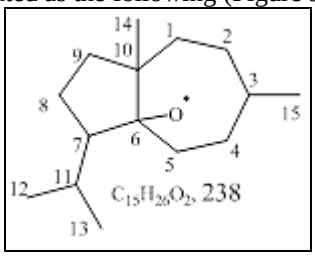

Figure 5: Main structure of the unknown component

There still exists oxygen. Owing to the ion peak as 220 (M-18) and 210 (M-28) is very weak, the 238 (68) shows that the structure is stable, and the unsaturated index is 3, taking account these, the oxygen in the structure should not exist as hydroxyl or carbonyl. The most reasonable linkage is forming an oxygen-oxygen bond, and to form a cycle, the most probably linkage position is with carbon 2 or 3, like the following (Figure 6).

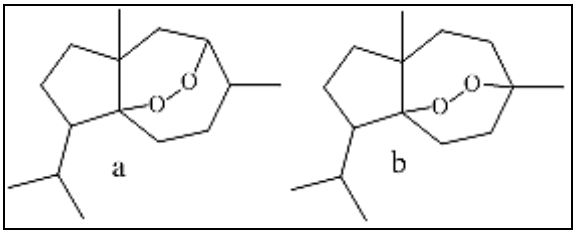

Figure 6: The most probably structure of unknown component

The fragment ion peak 206 (M-32) to lost O_2 doesn't existed, which is not like the compound as artemisinin which is easily to lost O_2, but there has such probability that doesn't lost O_2 like the compound as hanalpinol (Figure 7).

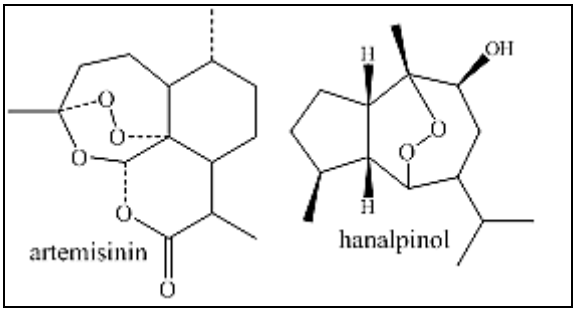

Figure 7: The structure of artemisinin and hanalpinol

CONCLUSION

In conclusion, in present, the most probably structure is listed in Figure 8, or the structure that has close relationship with them. The main dissociations of structure in Figure 9 is listed below.

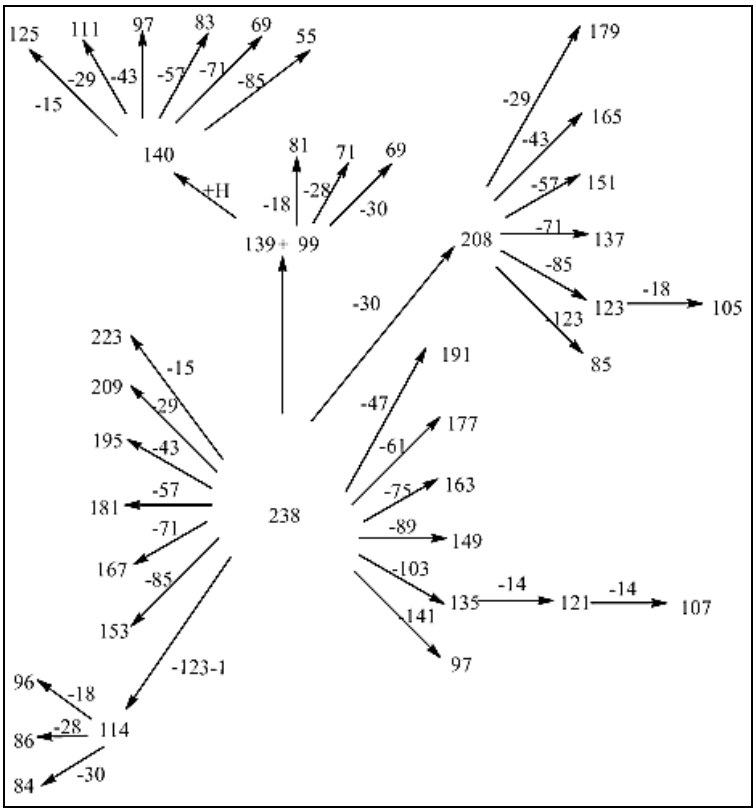

Figure 8: The main decomposition way of unknown component

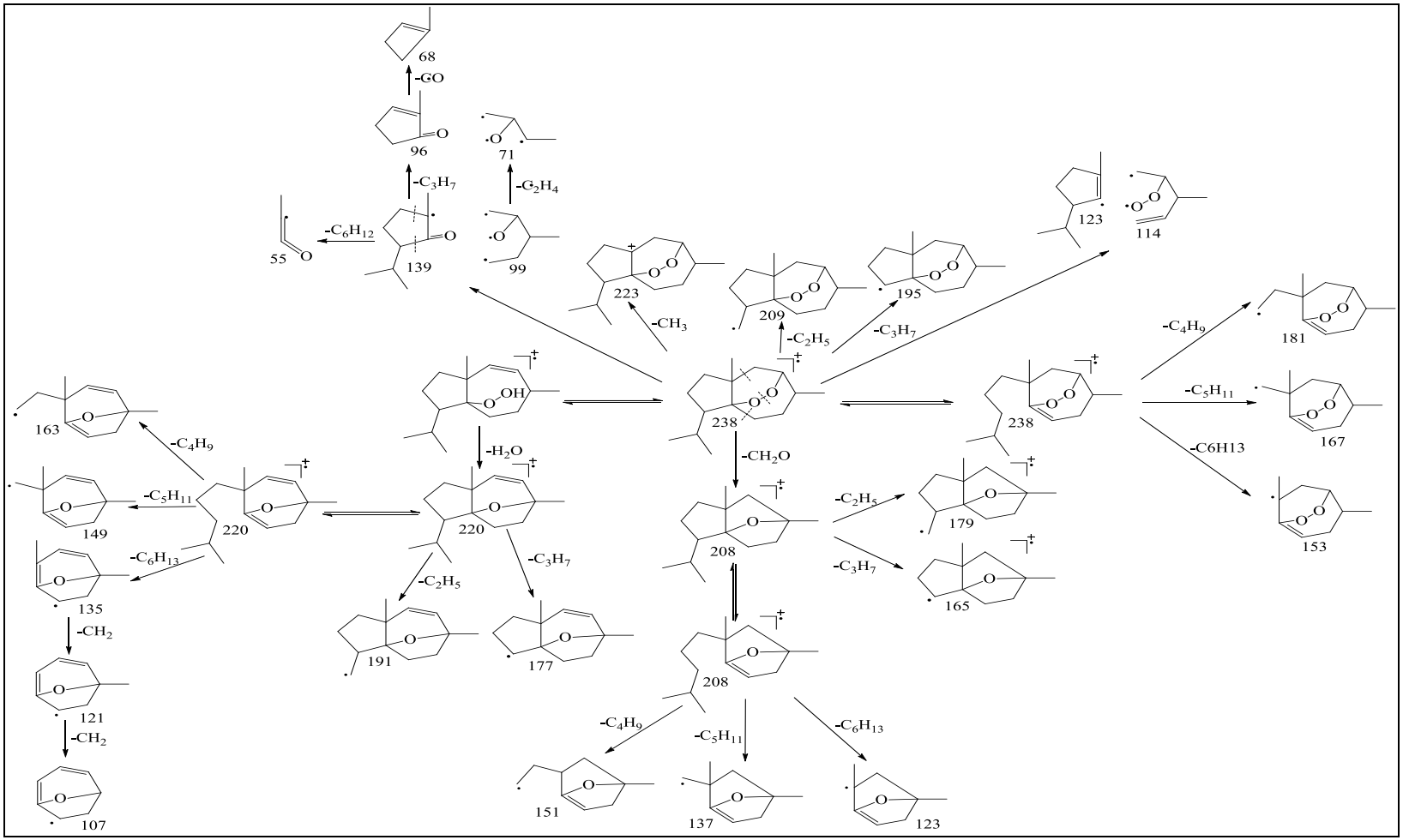

Figure 9: The main dissociation pathway of structure A

The exact structure will be elucidated by the ^{1}H-NMR (nuclear magnetic resonance) and ^{13}C-NMR if the compound can be isolated from the essential oil in the following research.

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