

研究論文

004 *The Reduction on Guaiazulene by  
the Bouveault-Blanc's Method*

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From the fragmentation patterns of hydrogenated guaiazulene by the Bouveault-Blanc's method, it has been presumed that the products were reduced from seven membered ring differed from the reduction in liquid-ammonia and had the following structures; 5,6 (or 6,7)-di-, 4,5,6,7 (or 5,6,7,8)-tetra- and 4,5,6,7,8,9 (or 4,5,6,7,8,10)-hexahydroguaiazulene.

A number of polarographic studies on azulene have been reported by Chopard-dit Jean and Heilbronner<sup>1)</sup> to reveal that azulene exhibited generally three reduction waves at about -1.7, -2.4 and -2.7 volt and the formation of anion at the first halfwave potential was reversible and further alkyl substitutions on nucleus resulted in a difficulty of the reduction, by Zuman<sup>2)</sup> to supplement that azulene cation was reduced at a higher voltage than the first potential and also by Given<sup>3)</sup> that a product of three electrons reduction was doubly protonated at 4 and 5 position to form a cyclopentadienyl anion, which was fairly stable because of its six  $\pi$  electron system.

On the other hand, Hafner<sup>4)</sup> reported a formation of 1,6-dihydroazulene by reduction of azulene with sodium-liquid ammonia and Fenton and Hurwitz<sup>5)</sup> commented on a synthesis of 5,6-dihydroazulene by condensation of cyclopentadiene with gultardialdehyde, though Bertelli and Crabtree<sup>6)</sup> proposed a structure of 1,6-dihydroazulene for this adduct from its nmr spectra. By Ruzicka and Rudolph<sup>7)</sup> a reduction product of chamazulene using sodium-amylalcohol was postulated to be decahydrochamazulene only on the basis of its elementary analysis. In Bouveault-Blanc's reduction with alcohol of rather less reactivity and sodium approvingly<sup>8)</sup>, an isolated double bond was not reduced<sup>9)</sup> but a conjugated double bond was hydrogenated at 1 and 4 positions with sodium-ethanol differed in each other whether at its boiling point or in liquid-ammonia.<sup>10)</sup>

The authors carried out the reduction of guaiazulene with sodium-ethanol and the reaction product was analysis by gas chromatography, nmr and mass spectra.

## Results and Discussion

**Gas chromatography:** Previously, the authors<sup>11)</sup> experienced that the retention time of a product obtained from guaiazulene by catalytic hydrogenation using Pt-C catalyst became

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shorter as hydrogenation proceeded. In this case, five peaks beside that of guaiazulene itself were observed at retention time of 5.0, 5.5, 6.5, 8.5 and 10.3 min. regardless of quantity of sodium used. However, it was found that the peak of dihydroguaiazulene decreased, in contrast with this the peak of tetrahydrocompound increased together with the time elapsed. Accordingly, the comparison of those corrected yield in Fig. 1 get into trouble, but the relation of weight of used sodium and relative intensities of those peaks were illustrated in Fig. 1.

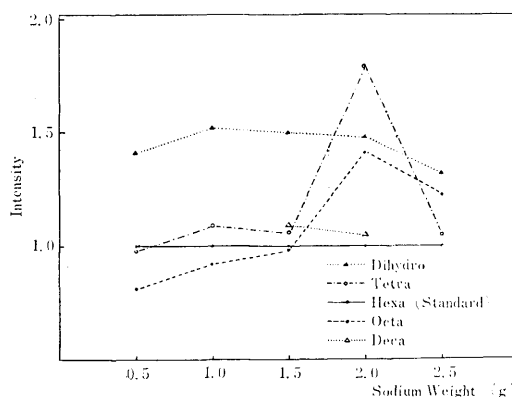


Fig. 1 Peak Intensities of Hydro-guaiazulene in Gas Chromatography

Assignment of peaks was also supported by mass spectrometry as described later, and three fraction corresponding to hexa-(1), tetra-(2) and dihydroguaiazulene (3) were isolated by using preparative gas chromatography under manual operation, though any of them was extremely contaminated by other components. Other two highly hydrogenated components could not be isolated because of their peaks having the close retention time.

**Mass Spectra:** As shown in Fig. 2, three major components corresponding to hexa-, tetra- or dihydroguaiazulene of each fraction 1, 2, 3 or the mixture of octa- and decahydroguaiazulene from the catalytic hydrogenation was revealed to have parent peak of  $m/e$  204, 202, 200 or 206 and 208, by comparing spectra of guaiazulene and others. And as observed commonly in their fragmentation patterns, the first fragment peak, smaller by  $m/e$  43 ( $\text{CH}_3\text{-}\dot{\text{C}}\text{H-CH}_3$ ) than parents', was generally most intense and was followed by serial peaks which were constituted of six, four and three peaks with interval of  $m/e$  14 ( $-\text{CH}_2-$ ), respectively. On the base of these facts, major component in fraction 1; hexahydroguaiazulene, 2; tetrahydroguaiazulene 3; dihydroguaiazulene and partial ion structure of minor components in fraction 1 were designated as shown in Fig. 3.

**NMR Spectra:** As mentioned above, Bertelli and Crabtree studied on hydrogenated chamazulene to determine their structures, especially sites of saturation by nmr. However, such a technique did not provide any distinct information with the product because of its poor

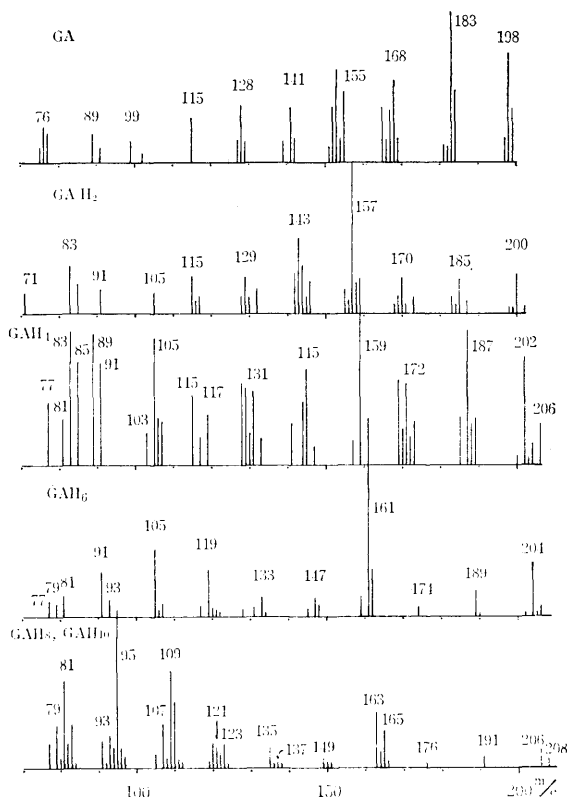
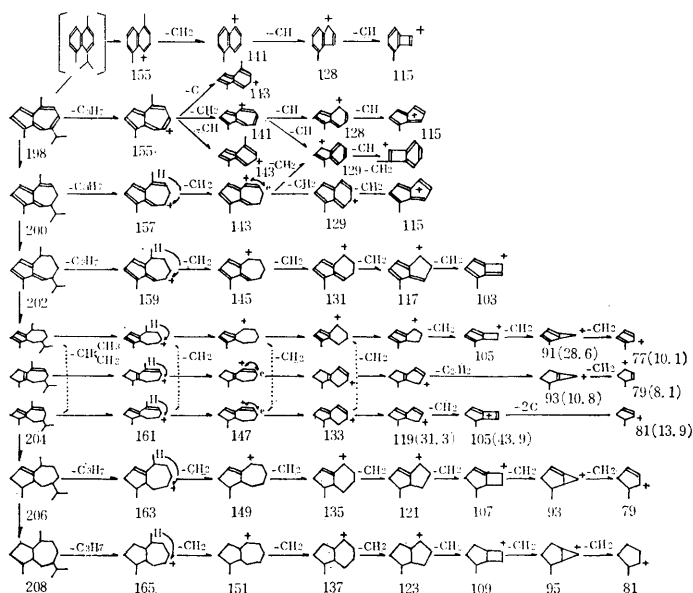


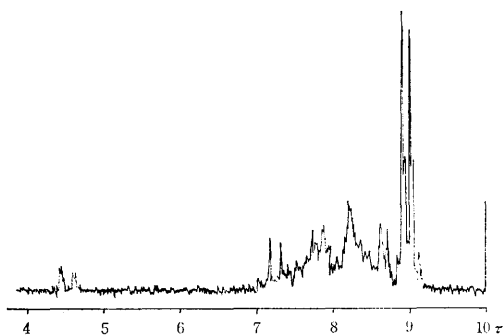
Fig. 2 Mass Spectra of Guaiazulene and Hydroguaiazulene



**Fig. 3** Presumed Fragmentation of Guaiazulenene and Hydroguaiazulene (Relative Intensities in Hexahydrocompound are indicated by a Parenthesized figure)

purity, expect with the fraction 1 as shown in Fig 4, two ethylenic protons on five membered ring were designated for signal of 4.15 and 4.16 in  $\tau$ , and other protons of saturated portion were observed in higher  $\tau$  values just as expected.<sup>12)</sup>

The following presumption has been designed to hold from the above observation; by Bouveault-Blanc's reduction guaiazulene was converted into di-, tetra- and hexa-, and presumably also into octa- and decahydroguaiazulenes, successively. Among them, as 1,6-dihydro structure for dihydro derivative was excluded owing to its characteristic fragmentation pattern and as cyclopentadienyl structure for hexahydro derivative was introduced owing to its informative nmr pattern, their major products were elucidated their structures rather confirmatively to be 5, 6- or 6, 7-di- and 4, 5, 6, 7, 8, 9 (or 10)-hexahydroguaiazulene, respectively. And by analogous speculation, tetrahydro derivative was assumed to be 4, 5, 6, 7- or 5, 6, 7, 8-tetrahydroguaiazulene.



**Fig. 4** NMR Spectra of Hexahydroguaiazulene fraction

## Experimental

Two grams of sodium was gradually added to a solution of two grams of guaiazulene (mp 130-131°) in 100 *ml* ethanol. After sodium disappeared ethanol was distilled off. Products were extracted with ether and were washed several times with water. The solution was

dried and ether was removed, then its acetone solution was subjected gas chromatography.  
(Silicon DC-550, 80-100 mesh, temp. 160°, He 1.0 Kg/cm<sup>2</sup>)

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