Vol. 12. (1975)

論　　文

003 *The Reaction of Isoguaiazulene with Maleic Anhydride or Acrylic Acid*

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(Received Sept 6, 1975)

The adducts produced by the reaction of isoguaiazulene with maleic anhydride or acrylic acid were inspected on the linked situation by various spectra. As the results, the production of abnormal adducts combined to 1 position in isoguaiazulene were surmised.

It has been reported by Treibs[1] that azulenyl-1-succinic acid and isoguaiazlenyl-1-succinic acid were obtained from the reaction of azulene and isoguaiazulene with maleic anhydride followed by hydrolyzed.

Itoh and others[2], the authors[3] have reported the formation of 3-[3-(7-isopropyl-1,4-dimethyl azulenyl)] succinic anhydride and 3-[3-(7-isopropyl-1,4-dimethyl azulenyl)] propionic acid from the reaction of maleic anhydride and acrylic acid with guaiazulene.

In present experiments, isoguaiazulene was allowed to react with maleic anhydride or acrylic acid in boiled water bath as in the case of guaiazulene. the purification of adducts by column chromatography filled silica gel yielded only oily products corresponded to adducts inspected by visible region, infra red, mass and nmr spectra were obtained.

1 Sample

Isoguaiazulene produced by the dehydrogenation of guaiol with selenium held about 6% impurity detected by gas chromatography. The impurity was not completely removed by the repetition of column chromatography and its molecular formula $C_{16}H_{20}$ corresponded to isoguaiazulene plus a methyl group was confirmed with mass spectra. Visible region, infra red, mass and nmr spectra of sample shown in Fig. 1, 2, 3 and 4.

2 Maleic anhydride adduct

The crystalline adduct was not produced in this experiment unlike guaiazulene. Therefore, the reactant was fractionized to 3 parts of blue, dark bluish violet and brown hard elution layer by the repetition of column chromatography. Since the blue fraction agreed with isoguaiazulene from visible region spectra, only dark bluish violet fraction was purified and was obtained visible region, infra red, mass and nmr spectra as shown in Fig. 1, 2, 3 and 4.

3 Acrylic acid adduct

An adducts were treated as the above on account of the oily state. The four fractions of blue (isoguaiazulene), dark violet, brownish violet and brown hard elution layer were obtained, the purification of both fractions of dark violet and brownish violet layer were repeated and measured visible region, infra red, mass and nmr spectra shown in Fig. 1, 2, 3 and 4.

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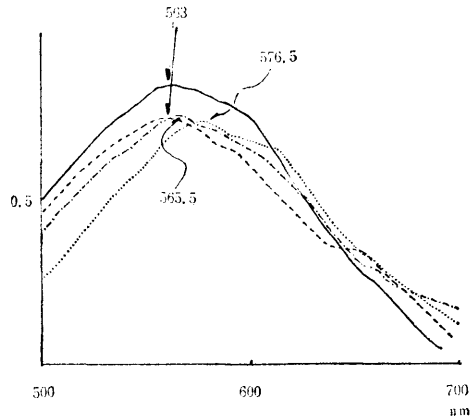

Fig. 1 Visible regions Spectra of Isoguaiazulene and Adducts.
- - - - isoguaiazulene (563 mm)
——— maleic anhydride adduct (563)
····· acrylic acid adduct (3-) (576.5)
-·-·-· // // (2-) (565.5)

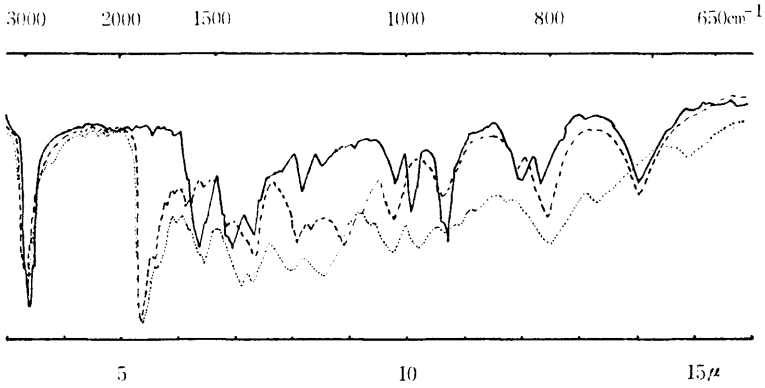

Fig. 2 Infra red Spectra of Isoguaiazulene and Adducts.
——— isoguaiazulene
- - - - maleic anhydride adduct
····· acrylic acid adduct
(2-,3-position adducts ··· almost the same)

Results and Discussion

The calculation value of adducts as carboxylic derivative in visible region spectra coincided almost with the observation value, practicaly, the existence of carbonyl or carboxyl group in adducts has shown in those infra red spectra. The disapearnce of a proton either of 1 or 3 position on isoguaiazulene nucleus in adducts was indicated from nmr spectra, accordingly the combinaton of dienophile to 1 or 3 position, namely an abnormal linkage was confirmed. On the other hand, the adduct combined two molecules to 1 and 3 positions was not obtained in this experiment. Two varied adducts seems to combined on 2 or 3 position of acrylic acid were presumed by mass spectra, dark violet and brownish violet adducts correseponded to each compounds combined to

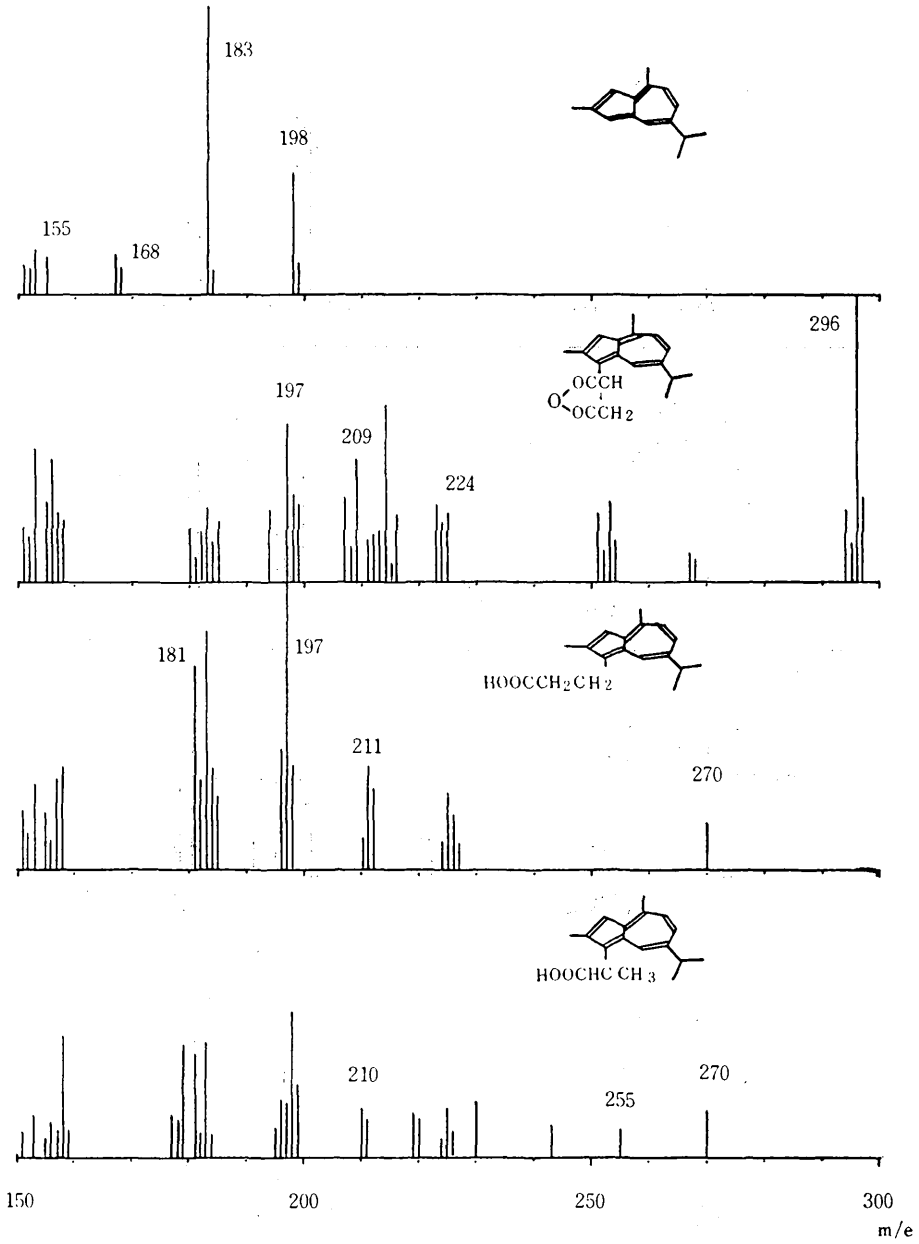

Fig. 3 Mass Spectra of Isoguaiazulene and Adducts.

2 or 3 position. The determination of reacted position can't decided from the above facts, but it has presumed that 1 position of a smaller steric hindrance was regard as most appropriate for the structure of isoguaiazulene. Accordingly, the production of following named adducts, 3-〔1-(7-isopropyl-2,4-dimethyl azulenyl)〕 succinic anhydride, 3-〔1-(7-isopropyl-2,4-dimethyl azulenyl)〕 propionic acid and 2-〔1-(7-isopropyl-2,4-dimethyl azulenyl)〕 propionic acid were surmised.

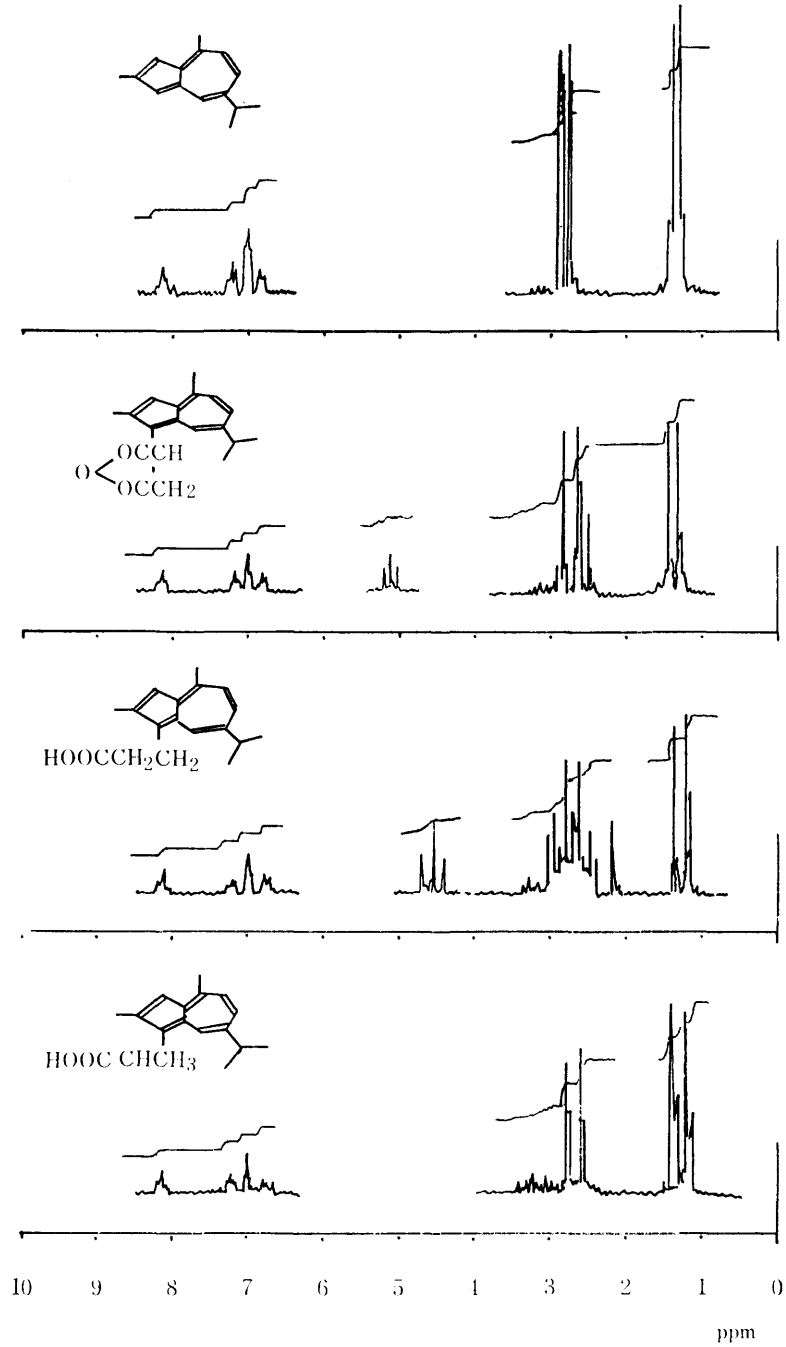

Fig. 4 NMR Spectra of Isoguaiazulene and Adducts.

Experimental

Apparatus

Infra red spectra.	Beckmann R-5 spectrometer.
Visible region spectra.	Hitachi 124 spectrometer.
Gas chromatography.	Hitachi K-23. PEG 20M, column 2*m*, He 1.3*Kg/Cm*², 180°.
Isoguaiazulene.	Picrate mp 110–11.5°. Retention time ; isoguaiazulene 3.8*min* impurity 4.2*min*.

Reaction,

1. In a 50*ml* flask, fitted with a 1*m* glass tube, was plased 0.2*g* of isoguaiazulene and 0.148*g* of maleic anhydride. The mixture was heated in boiling water bath for two hours, and was left throughout the night. Then, adduct were divided by column chromatography (Filler ; silica gel 60~80 and 100~200 mesh, mixed ratio 1 : 1. dia., 3*Cm*, length 45 *Cm*.). **2.** 0.3*g* of isoguaiazulene and 0.164*g* of acrylic acid were treated with similar method in above mentioned. Yield ; 120*mg* in **1**, 132*mg* (added to 3 position) and 48*mg* (2-) in **2**.

Reference

1) W. Treibs, Naturwissenschaften, **47**, 156 (1960)
2) S. Itō, H. Takeshita, T. Makino, Bull. Chem. Soc. Japan, **44**, 1982 (1971)
3) I. Ogura, K. Sato, M. Yamaguchi, Y. Ohtani, Yakugaku Zasshi, **91**, 1377 (1971)