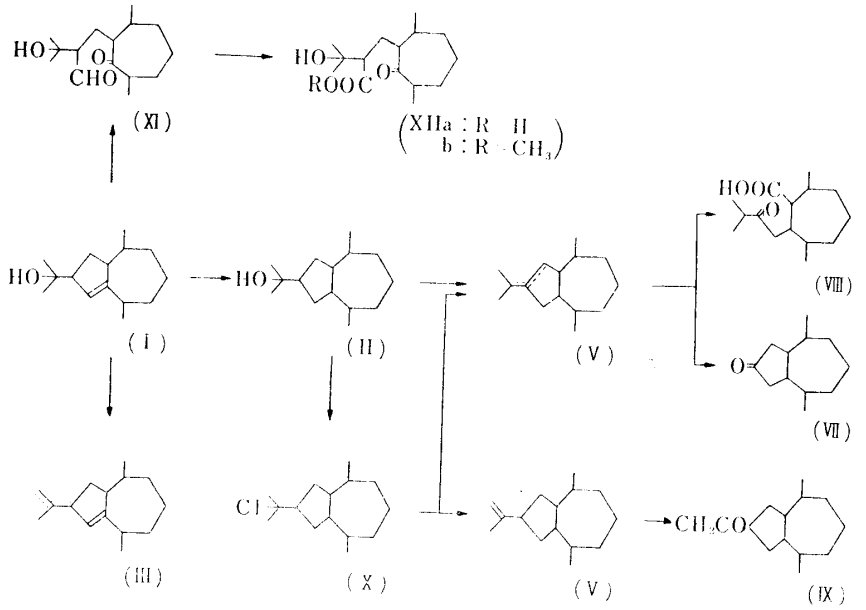
UDC 547.91:582.998

Structure of Hinesol

The so-called "atractylol," isolated from the rhizomes of *Atractylodes lancea* DE CANDOLLE, has been recognized as a mixed crystal of eudesmol and a new sesquiterpenoid monoëne alcohol, hinesol (I), $C_{15}H_{26}O$.[1] (I) possesses a vetivane skeleton and was readily dehydrated by formic acid, potassium hydrogensulfate, or hydrogen chloride with the formation of a hydrocarbon, hinesene (IIIa-c), which was shown to have a conjugated diene system in the molecule. Thus, the hydroxyl group and the ethylenic linkage must be situated at the allilic or homoallilic position.[2]

Ozonolysis of isodihydrohinesene (Va), obtained by formic acid dehydration of dihydrohinesol (II), afforded acetone, 2,6-dimethyl-bicyclo[5.3.0]decan-9-one (VII), $C_{12}H_{20}O$ (2,4-dinitrophenylhydrazone, m.p. 212~214°), and 2,6-dimethyl-7-isobutyroylmethylcycloheptane-1-carboxylic acid (VIII), $C_{15}H_{26}O_3$ (semicarbazone, m.p. 203~204°). When (II) was converted into the chloride (X) and treated with either aniline or ethanolic potassium hydroxide, isodihydrohinesene (Vb or Vc) was formed. Oxidation of (Vb) or (Vc) with ozone yielded, in addition to acetone, (VII), and (VIII), formaldehyde and 2,6-dimethyl-9-acetylbicyclo[5.3.0]-decane (IX), $C_{14}H_{24}O$ (2,4-dinitrophenylhydrazone, m.p. 143~144°). (IX) was reacted with methylmagnesium iodide to give an alcohol which was found to be identical with (II) in infrared absorption spectrum. These experiments furnished the evidence for the position of the tertiary alcoholic grouping to be in the isopropenyl side-chain. The infrared spectra of (IIIa-c) did not always indicate the strong absorption of vinylidene.



On the other hand, treatment of (I) with phosphoryl or thionyl chloride in pyridine afforded hinesene (IIId or IIIe) which exhibited a strong band due to the isopropenyl group but no longer showed the absorption characteristic of a conjugated diene system, both in the infrared and ultraviolet spectra. Hydrogenation of (I) in the presence of platinum catalyst in acetic acid yielded (II) and no product of hydrogenolysis. Ozonization of (I) gave hydroxyketoaldehyde (XI) which contained neither methyl-keto grouping nor active methylene. The methyl ester (XIIb) of keto-acid (XIIa), obtained by oxidation of (XI), was reduced to the triol (XIII) with lithium aluminium hydride but was not reduced with sodium

1) I. Yosioka, S. Takahashi, H. Hikino, Y. Sasaki : This Bulletin, **7**, 319 (1959).
2) I. Yosioka, H. Hikino, Y. Sasaki : *Ibid.*, **7**, 817 (1959).

borohydride. The oxidation of (I) was carried out with potassium permanganate to give the triol (XIV), m.p. 121.5~122°. When oxidized with periodate, (XIV) consumed only one equivalent of the reagent and did not produce acetone. From these facts it follows that (I) possesses the structure of 2,6-dimethyl-9-(1′-methyl-1′-hydroxyethyl)-bicyclo[5.3.0]dec-7-ene. Examinations on the configuration of compounds of this series are in progress.

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On the Mechanism of Enzymic Conversion of 6,7-Dimethylribolumazine to Riboflavin

The writers previously reported that a crude enzyme prepared from the mycelium of *Eremothecium ashbyii* reacted with 6,7-dimethylribolumazine to produce 6-methyl-7-hydroxyribolumazine besides riboflavin[1] and that the reaction yielded a considerable amount of riboflavin without any carbon donor.[2] The greater part of the products in this reaction were identified by paper partition chromatography and, of the two unidentified spots, the bluish green fluorescent one at Rf 0.10 was found to resemble the polymer consisting of two moles of 4-ribitylamino-5-aminouracil[3] reported by the present writers.

Recently, Plaut[4] discussed the conversion of 6,7-dimethylribolumazine to riboflavin by means of the enzyme of *Ashbya gossypii*, the gist of which is as follows: 1) The enzyme acts on 6,7-dimethylribolumazine to produce riboflavin without any carbon donor; 2) a C_4 compound is split off from the pyrazine ring of 6,7-dimethylribolumazine and then reacts with another 6,7-dimethylribolumazine to produce riboflavin. In other words, 6,7-dimethylribolumazine acts as a carbon donor as well as a carbon acceptor; 3) one mole of riboflavin is produced from two moles of 6,7-dimethylribolumazine; 4) when the methyl groups at the 6- and 7-positions of 6,7-dimethylribolumazine are labeled with ^{14}C, the molar specific radioactivity of the resulting riboflavin becomes twice as strong as that of 6,7-dimethylribolumazine; 5) decompositon by the Kuhn-Roth method of the riboflavin thus obtained gives two moles of acetic acid containing ^{14}C, thereby revealing the distribution of radioactivity in riboflavin. In another paper,[5] Plaut stated that formation of 1 mole of riboflavin requires 3 moles of 6,7-dimethylribolumazine and that 6-methyl-7-hydroxyribolumazine was a product other than riboflavin, but did not mention the amount of the resulting 6-methyl-7-hydroxyribolumazine in the above-mentioned report.[4]

The writers prepared an enzyme solution from *Er. ashbyii* and allowed the product to react with 6,7-dimethylribolumazine as reported before. A part of the reaction mixture

1) S. Kuwada, T. Masuda, T. Kishi, M. Asai: This Bulletin, **6**, 618 (1958).
2) S. Kuwada: Vitamins (Kyoto), **14**, 933 (1958).
3) S. Kuwada, T. Masuda, T. Kishi, M. Asai: This Bulletin, 8, 798 (1960).
4) G. W. E. Plaut: J. Biol. Chem., **235**, PC 41 (1960).
5) *Idem*: Federation Proc., **19**, 312 (1960).