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The Structure of Yellow Pigment from the Rhizomes of *Cimicifuga dahurica* Maxim.

Two yellow pigments were isolated from the rhizomes of *Cimicifuga dahurica* Maxim. (Ranunculaceae) and were elucidated as 3-(3′-methyl-2′-butenyliden)-2-indolinone. The two were shown to be geometrical isomer each other and ethanolic solution of one of them gave colorless substance on standing, which was regarded as a product of dimerization.

Keywords——yellow pigment; *Cimicifuga dahurica* Maxim.; isatin; 3-(3′-methyl-2′-butenyliden)-2-indolinone; 3-(3′-methylbutyl)-2-indolinone; UV of 2-indolinones; UV of 3-indolinones

The Chinese drug "Bei-shengma (北升麻)," the rhizomes of *Cimicifuga dahurica* Maxim. (Ranunculaceae), has been shown to afford phenolic acids, such as isoferulic acid,[1] triterpenes,[2] and chromones, *e.g.* visamminol, visnagin and so on.[3] The authors have recently found the presence of several yellow pigments in this rhizomes by means of thin-layer chromatography and have tried to isolate these substances, obtaining a product of yellow needles (I) together with a small quantity of an analogous compound (II). This paper deals with the structure elucidation of these products.

The ethyl acetate extract of the crude drug, obtained from the Tiăn-jin (天津) market, was chromatographed over silica gel using hexane–ethyl acetate (3: 1) as the solvent. The latter half of the eluate upon rechromatography over alumina followed by elution with hexane–ethyl acetate (2: 1) gave I and II.

The compound I, mp 200—203°, was assigned the molecular formula $C_{13}H_{13}NO$ on the basis of analytical and mass spectral data. I is insoluble in aqueous hydrochloric acid and gives no reaction with Dragendorff's test solution. The infrared spectrum of I is suggestive of the presence of NH and lactam carbonyl groups as well as aromatic ring. The proton magnetic resonance (PMR) spectrum of I shows signals which can be assigned to the groups of $=C(CH_3)_2$ (δ 2.07, s), =CH–CH= (δ 6.77, 7.59. d, J=12 Hz), NH (δ 8.33, broad s) and four aromatic protons (δ 6.9—7.6, m).

Ozonolysis of I led to the formation of red crystalline product (III), mp 198—199°, which was identified as isatin by the melting point determination on admixture with an authentic sample. The spectral data of III are also superimposable with those of the authentic sample. Furthermore, acetone was identified on oxidation of I with chromic acid in acetic acid. On the basis of this evidence and the spectral data, two possible structures, 3-(3′-methyl-2′-butenyliden)-2-indolinone (Ia) or 2-(3′-methyl-2′-butenyliden)-3-indolinone (Ib) were given for I.

The catalytic hydrogenation of I using Adams, catalyst gave a product of colorless viscid oil (IV), whose PMR spectrum exhibits, in addition to peaks arising from the protons of 2-methylbutyl group and those of 1,2-disubstituted benzene ring, a triplet at δ 3.40 attributable to a methine proton resulted from the hydrogenation. The chemical shift of this triplet is very similar to that of the signal due to the benzylic methine proton appearing in the PMR spectrum of α-phenylpropionic acid,[4] while the methine proton of tryptophan has been known to be visible at δ 4.5 in its PMR spectrum,[5] indicating that 3-(3′-methylbutyl)-2-indolinone

1) T. Inoue, C. Nakata, and K. Izawa, *Shoyakugaku Zasshi*, **24**, 76 (1970).
2) N. Sakurai, T. Inoue, and M. Nagai, *Yakugaku Zasshi*, **92**, 724 (1972).
3) M. Ito, Y. Kondo, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **24**, 580 (1976).
4) C.J. Pouchert and J.R. Campbell (eds.), "The Aldrich Library of NMR Spectra," Vol. 10, Aldrich Chemical Company, Inc., Milwaukee, 1974, p. 133.
5) *Idem, ibid.*, Vol. 8, p. 68.

(IVa) derived from Ia is preferable for the structure of IV to 2-(3′-methylbutyl)-3-indolinone (IVb) formed from Ib.

Further evidence for this structural assignment was provided from the facts that the ultraviolet (UV) spectrum of IV, λ_{max} nm (log ε): 209 (4.395), 250 (3.968), 279 sh (3.208), is extremely similar to that of 3-methyl-2-indolinone, λ_{max} nm (log ε): 207 (4.437), 247 (3.940), 278 sh (3.158),[6] whereas 3-indolinone derivative has been known to give the UV spectrum, λ_{max} nm (log ε): 230 (4.439), 256 sh (3.778),[7] which is entirely different from those of 2-indolinones.

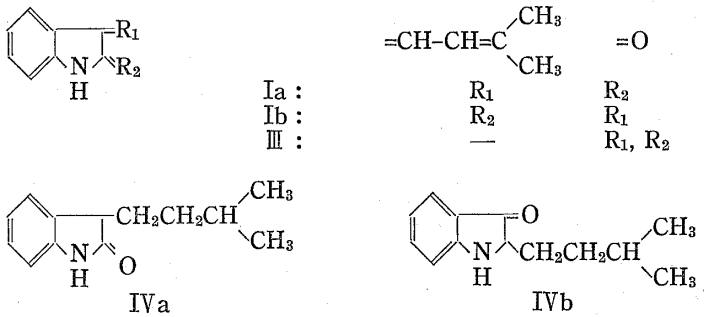

Fig. 1

Thus, the structure of I was established as 3-(3′-methyl-2′-butenyliden)-2-indolinone (Ia).

The compound II, mp 213—214°, gives spectral data very similar to those of I, and on ozonolysis gave III. II was shown to be a geometrical isomer of I from the facts that I on heating with dilute alkali in ethanolic solution converted into II resulting in the formation of a mixture of the both compounds and the reverse reaction from II was also observed to occur narrowly, and that hydrogenation of II gave the product identical with that formed from I. Furthermore, the ethanolic solution of II on standing deposited a hardly soluble substance of colorless solid, while the formation of this substance from I was not observed under the same conditions.

In view of the fact that 3-methylen-2-indolinone has been known to undergo dimerization by Diels-Alder reaction forming a colorless solid in various solvents,[6] the colorless product from II could be regarded as a dimer formed by an analogous process. It seems that in the case of I the 3-methyl-2-butenyliden side chain would be arranged so as to effect a steric hindrance, interfering with the dimerization.

The geometric configuration of I and II, and the structure of the colorless product from II, probably a dimer, are now under investigation. There is no record in the literature of natural occurrence of these pigments, though synthetic formation of a compound to which the structure Ia was assigned has been reported.[8] However, no detailed data of this compound can be found in the literature.

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Osaka College of Pharmacy
2-Kawai, Matsubara,
Osaka, Japan

Kiyoshi Hata
Kimiye Baba
Mitsugi Kozawa

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6) R.L. Hinmam and C.P. Bauman, *J. Org. Chem.*, **29**, 2431 (1964).
7) A.I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, Oxford, 1964, p. 175.
8) G. Cardillo, L. Merlini, and S. Servi, *Annali di Chimica*, **60**, 564 (1970).