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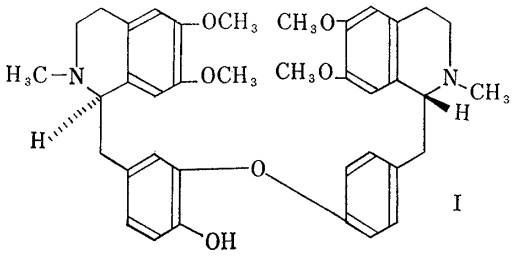
Richard H. F. Manske,*1 Masao Tomita, Kazuyoshi Fujitani, and Yasuko Okamoto*2 : Studies on the Alkaloids of Menispermaceous Plants. CCXIX.*3 Dauricine from *Menispermum canadense* L.

(*Research Laboratories, Dominion Rubber Co., Ltd.*1 and Faculty of Pharmaceutical Sciences, Kyoto University*2)

Dauricine, a tertiary phenolic biscoclaurine type alkaloid, was first isolated in an amorphous state from *Menispermum dauricum* DC. by Kondo and Narita,[1] and its occurrence in *M. canadense* L. collected in Hokkaido[2] and in Canada[3] was reported, though the direct comparison of the specimen of Canadian base with that of Japanese origin had not been made.



I

Thereafter, extensive degradative and synthetic studies on the base have made it clear that the structure of dauricine is represented by formula I.[4]

Recently, it has been reported that dauricine is crystallizable in the form of its chloroform adduct, and that amorphous dauricine contained an amount of bases that are closely related to dauricine in structure.[5]

The authors carried out a re-examination of the amorphous dauricine[3] isolated from the rhizome of *M. canadense* L. collected in Canada.

Chromatographic purification and separation of the base afforded a crystalline chloroform adduct, and this adduct was compared with dauricine chloroform adduct by mixed melting point determination, thin-layer chromatography,*4 optical rotation, infrared, and nuclear magnetic resonance spectra,*5 and it was confirmed that both were identical (Figs. 1, 2, and 3).

Additionally, it was found that the crude base also contained a small amount of unidentified bases, and their spectral data and color reaction suggested that they were phenolic and deme-

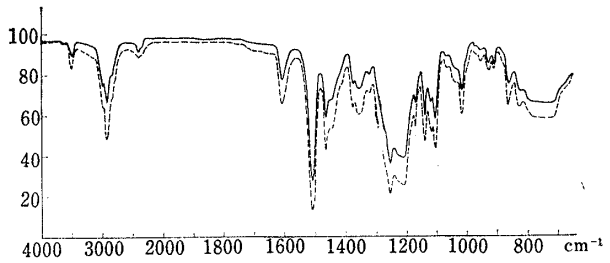


Fig. 1. Infrared Spectra (in $CHCl_3$)
——— Dauricine chloroform adduct
------- The crystalline adduct obtained from *M. canadense* L.

*1 Guelph, Ontario Canada.
*2 Yoshida-Shimoadachi-cho, Sakyo-ku, Kyoto (富田真雄, 冨士谷憲徳, 岡本靖子).
*3 Part CCXVIII, Y. Watanabe, H. Furukawa, M. Kurita : Yakugaku Zasshi, in press.
*4 Aluminiumoxyd G nach Stahl, solvent : $CHCl_3$-acetone (1:1), detected by Dragendorff's reagent.
*5 The NMR spectra were measured with a Varian A-60 spectrometer in $CDCl_3$, using tetramethylsilane as an internal reference.

1) H. Kondo, Z. Narita : Yakugaku Zasshi, **47**, 279 (1927).
2) H. Kondo, Z. Narita, M. Murakami : *Ibid.*, **61**, 375 (1941).
3) R. H. F. Manske : Can. J. Research, **21B**, 17 (1943).
4) M. Tomita : Fortschr. Chem. org. Naturstoffe, **9**, 192 (1952), Springer-Verlag, Wien; M. Tomita, K. Itoh, H. Yamaguchi : Pharm. Bull. (Tokyo), **3**, 449 (1955); M. Tomita, J. Kunitomo : Yakugaku Zasshi, **82**, 741 (1962).
5) M. Tomita, Y. Okamoto : Yakugaku Zasshi, **84**, 1030 (1964); *Idem* : *Ibid.*, **85**, 456 (1965).

thylated dauricine type, but they were not further investigated because of the scarcity of the material.

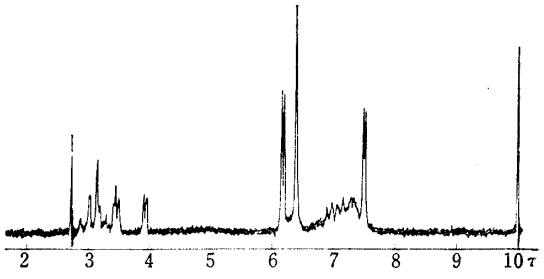


Fig. 2. NMR Spectrum of Dauricine $CHCl_3$ adduct in $CDCl_3$

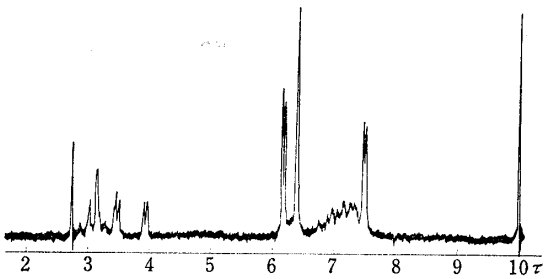


Fig. 3. NMR Spectrum of the crystalline adduct obtained from *M. canadense* L. in $CDCl_3$

Experimental*6

Dauricine Chloroform Adduct——Crude amorphous dauricine (1 g.) was dissolved in benzene and the insoluble matter was filtered off. The filtrate was chromatographed on deactivated alumina*7 (0.8×20 cm.), developed with benzene, then eluted successively with benzene, benzene-$CHCl_3$ (100:1), benzene-$CHCl_3$ (10:1), and $CHCl_3$. Fractions eluted with benzene-$CHCl_3$ (10:1) and $CHCl_3$ showed two spots on thin-layer chromatography*4 and the spots gave a blue coloration with Gibbs' reagent. Fractions eluted with benzene and benzene-$CHCl_3$ (100:1) were collected and the solvent was evaporated to give 300 mg. of colorless oil, which was crystallized from $CHCl_3$-hexane. Recrystallization from the same solvent gave colorless prisms, m.p. 96~100° (sint. 87°), $[\alpha]_D^{19}$ −115.1° (c=0.73, MeOH). NMR signals : 7.48, 7.52 τ (6H, 2×N-CH_3); 6.17, 6.20, 6.40 τ (12H, 4×O-CH_3); 2.88~3.96 τ (11H, aromatic H). These crystals were identical with the dauricine chloroform adduct[5] by comparison of mixed melting point, thin-layer chromatography, IR ($CHCl_3$, KBr), and NMR spectra. Picrate of this base resisted all attempts at crystallization and was obtained as a yellow amorphous powder.

Dauricine Dimethiodide——To a solution of 27 mg. of crystalline base obtained above in a small amount of MeOH was added 0.5 ml. of MeI and the mixture was allowed to stand at room temperature a few minutes, then the solvent was evaporated. The residue was recrystallized from MeOH-H_2O to yield 20 mg. of faint yellow needles, m.p. 195~198° (decomp.), $[\alpha]_D^{19.5}$ −137.5° (c=0.24, 50% MeOH). The IR spectrum (Nujol) was superimposable on that of an authentic sample of dauricine dimethiodide.[5]

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*6 All melting points were determined in a Yanagimoto Micro-melting Point Determination Apparatus.
*7 Aluminiumoxyd standardisiert nach Brockmann (E. Merck) which was suspended in a mixture of benzene-water (15:1) and allowed to stand for 2 days.