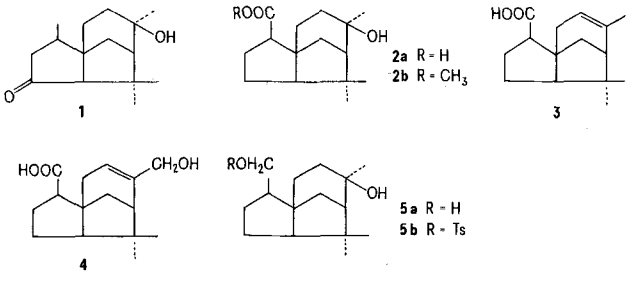
at 75–80°. The amorphous **3** exhibited trisubstituted double bond (1630 and 820 cm^{-1}), no maximum absorption above 205 nm in UV-spectrum, and NMR-spectrum signals at τ_{CDCl_3} 8.27 (3H, br s, CH_3—C=C—H) and



4.70 (1H, m, CH_3—C=C—H). Selenium dioxide oxidation of **3** in boiling ethanol gave **4**, m.p. 155–156°; ν_{max} 3400 cm^{-1}(—OH); τ_{CDCl_3} 6.00 (2H, br s, —CH_2OH).

By treating **2a** with CH_2N_2 in MeOH gave a methyl ester **2b**, m.p. 90–100°, ν_{max} 3270, 1730, and 1710 cm^{-1}; its NMR-spectrum exhibits signal at τ_{CDCl_3} 6.37 (3H, s, —$COOCH_3$), which was stable to alkali indicating that the carbomethoxy group was in a stable configuration. The reduction with LAH in THF methyl ester afforded a sole product **5a** (m.p. 133–135°) which expressed strong hydroxyl absorption (3270 cm^{-1}) instead of ester absorption. The conversion of diol **5a** to tosylate **5b** (m.p. 70–71°) was accomplished by the interaction with tosyl chloride in dry pyridine. **5b** on subsequent reduction with LAH afforded α-cedrol. From these results the structure of isocedrolic acid is represented by formula **2a**.

Extractive Components from the Nutmeg of *Myristica simarum* A. DC.: The Structure of Lignan-Ketone: Otobanone

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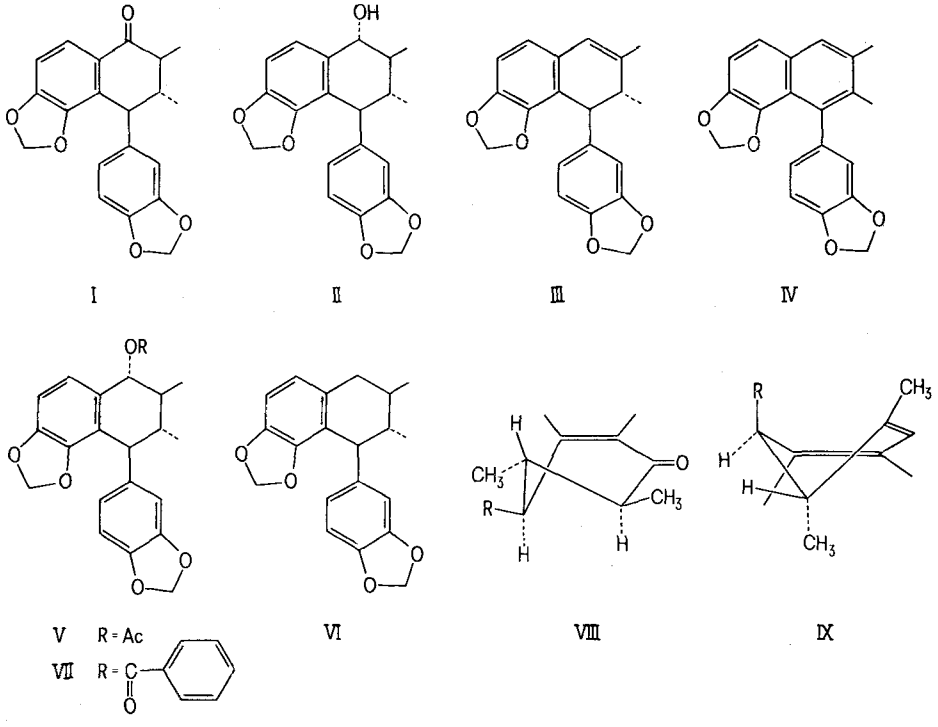
10 November 1975.

Summary. Otobanon obtained from *n*-hexane extract of *Myristica simarum* A. DC. was elucidated as 1-oxo-otobain by the physical spectra and chemical degradation.

In connection with our interests in lignans and in view of the potential of *Myristica* fragrans as a native drug[2,3], chemical studies on *Myristica cagayanensis* Merr.[4] and *Myristica simarum* A.DC. were undertaken in our laboratory. This report deals with the chemical constituents of nutmeg of *Myristica simarum* A.DC.

Freshly ground nutmeg was extracted with n-hexane at room temperature. The extract was concentrated and



the precipitated crystalline trimyristin, m.p. 54–56°, was filtered off. When the filtrate was chromatographed on a silica gel column, the crystalline otobanone was obtained, which was the same constituent from the extract of *Myristica cagayanensis* Merr.[4].

Otobanone (I), m.p. 175–176°, $[\alpha]_D$-27.1° (C. 0.7 in $CHCl_3$), $C_{20}H_{18}O_5$, λ_{max} 236 and 288 nm (log 4.35 and 4.00), exhibits IR-absorption bands at 3080, 1675, 1620, 1585, 1500, 1260, 1245, 1055 and 950 cm^{-1}. According to these data and NMR-data, otobanone must contain 2 secondary

methyl groups, 2 methylenedioxyphenyl groups and a benzoyl moiety.

Reduction of otobanone with $NaBH_4$ in MeOH afforded needle-like crystalline alcohol (II) which showed OH stretching absorption at 3320 cm^{-1}, but no absorption of a conjugated carbonyl group. Compound (II) was treated with *p*-tosylic acid in benzene under reflux, and gave a liquid (III) [ν_{max} 1630 and 810 cm^{-1}, no –OH absorption; λ_{max} 241, 273.5 and 281 nm (log ε 4.14, 4.15 and 4.19)]. Dehydrogenation of compound (III) by dichlorodicyanobenzoquinone produced a phenyl naphthalene derivative (IV) (m.p. 183–185°) which was identified with tetradehydrootobain[5]. Treatment of compound (II) with acetic anhydride in pyridine yielded an acetate (V), m.p. 139.5–140.5, ν_{max} 1720 cm^{-1}, which was treated by reaction with Zn in AcOH under reflux to give unexpected elimination product (III). Hydrogenation of (III) with 5% Pd-C in MeOH gave dihydro compound (VI) (m.p. 136–137°) which was identified as otobain[5]. The evidence concluded that otobanone had to be 1-oxo-otobain as drawn (I) or its C_2 epimer. Further evidence to confirm otobanone to be 1-oxo-otobain is that compound (I) or (V) afford otobain by the reaction of hydrogenolysis with 5% Pd-C.

The assignment of 1-hydroxyl in (II) is in α-quasi-equitorial orientation by the observation that C_1H (with great diquasiaxial coupling constant) exhibited at τ_{CDCl_3} 4.12 (J = 8 Hz) and τ_{CDCl_3} 3.76 (J = 9 Hz) in its acetate (V) and benzoate (VII) derivative, respectively.

Both the configuration and the conformation of ring B in otobanone are the same as that of otobain were defined by the NMR-spectrum. C_4H in otobanone shows great coupling constant at τ_{CDCl_3} 6.28 (J = 9.2 Hz), and the methylenedioxy-protons attached to ring A are markedly different. In otobanone, this is a proton of typical AB system in which the coupling constant is 1.2 Hz and the chemical shift is 0.1 ppm. This is to be expected from formula (I) provided that the conformation of ring B is pseudochair form (VIII), and that in this conformation the phenyl group is in quasi-equatorial. The conformation of ring B in (III) is obviously different from otobanone by the observation of its NMR-spectrum. C_4H in (III) shows less broad singlet at τ_{CDCl_3} 6.00 ($W_{1/2}$ = 3 Hz), and the methylenedioxy-protons attached to ring A exhibit equivalent at τ_{CDCl_3} 4.07 (the same chemical shift with other methylene-protons attached to ring C). This is to be expected from formula (III) provided that the conformation of ring B is an other pseudo-chair form (IX) and that in this conformation the phenyl group is in quasi-axial.

Compound (III) prefers conformer (IX) to conformer (VIII) ascribing to great steric hindrance between ring C and methylenedioxy group attached to ring A in latter conformer. The fact that acetate (V) or benzoate (VII) eliminates spontaneously in $CDCl_3$ solution for 6 days under room temperature to gave (III), is further proof.

[1] Acknowledgment. The authors are indebted to Chemical Research Center for financial support under the project No. CRC-6203, which supported by the National Council on Science Development of China.

[2] J. E. Forrest and R. A. Heacock, Lloydia *35*, 440 (1972).

[3] J. E. Forrest, R. A. Heacock and T. P. Forrest, J. chem. Soc. C *1974*, 205.

[4] Y. T. Lin, Y. H. Kuo and S. T. Kao, J. Chinese chem. Soc. *18*, 45 (1971).

[5] T. Gilchrist, R. Hodges and A. L. Porte, J. chem. Soc. *1962*, 1780.

Isolation of the Insect Paralyzing Agent Coniine from *Sarracenia flava*

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Summary. As part of a study to clarify the relationship between insects and the insectivorous plant *Sarracenia flava*, we have observed the presence of the paralyzing agent coniine in the volatile constituents. Fire ants have been used as the test organism in bioassay studies for paralyzing activity.

The pitcher plant, *Sarracenia flava*[4], has long been known to be insectivorous[5]. This characteristic, in conjunction with the conspicuous leaves and flowers, has stimulated interest among scientists in the unique relationship of this plant to the insect population[6]. A variety of insects (ants, wasps, bees, butterflies, moths) are known[5] to enter the pitcher where they are subsequently rendered helpless, digested, and absorbed. Lambert[7] has reported experiments, apparently made on fresh plants of *S. purpurea*, in which a volatile base was present which had the characteristic mouse-like odor of coniine. However, Lambert's attempt to isolate the base from the pitchers (leaves) failed because 'the base was present in so small an amount that only the odor was obtained'.

We have now confirmed the presence of coniine in the volatile fraction of *S. flava*. We have also demonstrated its insect paralyzing activity by administering coniine to fire ants. Fire ants in a small container were paralyzed within 30 sec when exposed to 100 ng of coniine. The insects died upon further exposure.

Isolation procedures. Sarracenia flava leaves were collected 14 miles due east of Panama City, Florida in June

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[4] The plant material used was identified as *Sarracenia flava* (Sarraceniaceae) by Dr. Sidney McDaniel, Department of Botany, Mississippi State University. A voucher (preserved) specimen (SM-16, 702) representing material collected for this investigation is available for inspection at the Herbarium of the Department of Botany, Mississippi State University.

[5] F. E. Lloyd, *The Carnivorous Plants* (Chronica Botanica Co., Waltham, Mass. 1942), p. 17.

[6] G. Lambert, Ann. Séanc. Acad. Sci., Paris *88*, 185, (1879). – J. S. Hepburn, Trans. Wagner Free Inst. Sci. *11*, 27 (1927).

[7] *The Merck Index*, 8th edn. (Merck and Co., Rahway, N.Y. 1968), p. 282.