This structure was confirmed synthetically by the method of Poizzi *et al.*[4] Refluxing an excess amount of diethyl-($\gamma\gamma$-dimethylallyl)-malonate (VI) with aminoveratrole gave the intermediate 6,7-dimethoxy-3-isopentenyl-4-hydroxy-2-quinolone (VII) which was cyclodehydrogenated to give demethyl oricine (VIII). *N*-methylation of demethyloricine gave a compound whose NMR and IR were superimposable on those of oricine (V).

EXPERIMENTAL

Isolation of oricine. The pulverized wood (14·75 kg) was extracted continuously for over 2 days with light petroleum (60–80°). Evaporation of the solvent afforded an oily material (300 g) which was chromatographed on alumina and a fraction eluted with 20% benzene in Et_2O gave a yellow crystalline substance, oricine. Recrystallization from benzene gave large, prism-like crystals (1·5 g) m.p. 150–152°, optically inactive. (Found C, 67·05, H, 6·2; $C_{17}H_{19}O_4N$ requires C, 67·17, H, 6·34%.) M^+ (from mass spectrum) 301 ν_{max} 1639 cm^{-1} (carbonyl of 2-quinolone).

Hydrogenation of oricine. Oricine (0·135 g) was dissolved in MeOH (50 ml) and Pt_2O (0 1 g) added. The mixture was shaken up with H_2 at atmospheric pressure until no more uptake. The filtrate was evaporated to give white crystalline, dihydrooricine m p. 150°. (Found C, 67·02, H, 6·81, $C_{16}H_{21}O_4N$ requires C, 67·32, H, 6·93%.) M^+ (from mass spectrum) 303.

Preparation of 6,7-dimethoxy-3-isopentenyl-4-hydroxy-2-quinolone. A mixture of aminoveratrole (3 g) and diethyl—($\gamma\gamma$-dimethylallyl)-malonate (6 g) in diphenyl ether (50 ml) was refluxed in N_2 for 5 hr. When cool, the solid 2-quinolone was precipitated with petrol (40°–60°), collected and washed. The solid was shaken with $CHCl_3$ and filtered to give an ash-coloured powder. Yield 1·8 g, m.p. 200°–201°. (Found: C, 66·51, H, 6·84%; $C_{16}H_{19}O_4N$ requires C, 66·42, H, 6·58%). M^+ (mass spectrum) 289. γ_{max} 1639 cm^{-1} (Carbonyl of a 2-quinolone).

Preparation of demethyl-oricine. 6,7-Dimethoxy-3-isopentenyl-4-hydroxy-2-quinolone (0·1042 g) and 2,3-dicyano-5,6-dichloro benzoquinone (DDQ) (0·1056 g) in dry benzene (100 ml) was refluxed for 4 hr. The mixture was cooled, filtered, evaporated and the residue extracted with $CHCl_3$, washed with 10% $NaHCO_3$ (*ca.* 500 ml) and H_2O. The $CHCl_3$ extract was dried (Na_2SO_4) and evaporated to give a crystalline substance m.p. 210°–212°. Yield (*ca.* 0 1 g). (Found: C, 68 01; H, 6 01%; $C_{16}H_{17}O_4N$ requires C, 67·92; H, 5 98%) M^+ (mass spectrum) 287.

Methylation of N-demethyloricine to oricine. *N*-demethyloricine (0 05 g), MeI (2 ml) K_2CO_3 (5 g) in acetone (40 ml) was refluxed for 6 hr on a steam bath. The filtrate was evaporated to give a residue which was taken up in $CHCl_3$, washed (H_2O), dried (Na_2SO_4) and evaporated to give oricine. Recrystallized from benzene, m.p. 150°. Yield (0 03 g). (Found: C, 67·51; H, 6·30%.) The IR and NMR spectra were identical with those of the authentic oricine.

[4] F Piozzi, P. Venturella and A. Bellino, *Gazz. Chim. Ital.* **99**, 711 (1969); *Chem. Abs.* **71**, 91709 (1969).

Phytochemistry, 1971, Vol 10, pp 3330 to 3331. Pergamon Press Printed in England.

NEUTRAL CONSTITUENTS OF *ORIXA JAPONICA*

HIROSHI ABE, TAKESHI KAWASHIMA,* ISAO MARUTA, MITSUAKI KODAMA and SHÔ ITÔ
Department of Chemistry, Tohoku University, Sendai, Japan

(*Received* 3 *June* 1971)

Plant. Orixa Japonica Thunb. *Uses.* Not known. *Previous work.* Alkaloids.[1]

Leaves. Extracted with MeOH, steam distillation. Chromatographed using Al_2O_3. *Bergapten.* $C_{12}H_8O_4$, m.p. 191–192°. M.p., mixed m.p., superimposable IR and NMR spectra. *Xanthotoxin.* $C_{12}H_8O_4$, m.p. 146–148°. M.p., mixed m.p., superimposable IR and NMR spectra. *Friedelin.* $C_{30}H_{50}O$, m.p. 260–261°. M.p., mixed m.p., superimposable IR and NMR spectra. *Isoarborinol.* $C_{30}H_{50}O$, m.p. 298–299°. M.p., mixed m.p., superimpos-

* On leave of absence from Kojin Co. Ltd.

[1] M. Terasaka, T. Ohta and K. Narahashi, *J Pharm. Soc Japan* **73**, 773 (1953), *idem. Chem. Pharm. Bull. Japan* **2**, 159 (1954) M. Terasaka, *ibid*, **8**, 523 (1960).

able IR, NMR and mass spectra. *Spathulenol.* $C_{15}H_{24}O$, liq., 3,5-Dinitrobenzoate, m.p. 148°. Superimposable IR and NMR spectra of the alcohol and IR spectra of the derivative. *Carvomenthol, α-Terpineol, α-* and *β-Pinene, Camphene, γ-Terpinene, Limonene, Cineol.* Identified by gas chromatography, superimposable IR and NMR spectra. *Unidentified compounds.* (*A*) $C_{15}H_{22}O$ (M^+), liq., IR $\nu^{liq.}$ 3500, 1653, 1060, 888 cm^{-1}, NMR δ^{CDCl_3} 0·5–0·9 (2H,m), 1·08 (6H,s), 1·13 (3H,s), 4·18 (1H,br.s), 4·95 (1H,br.s). (*B*) $C_{15}H_{24}O$ (M^+), liq., IR $\nu^{liq.}$ 3500, 1660, 1630, 1150, 1010, 770 cm^{-1}, NMR δ^{CDCl_3} 0·80 (3H,d, $J = 6·8$), 0·82 (3H,d, $J = 6·8$), 1·20 (3H,s), 1·65 (3H,s), 5·53 (1H,m). (*C*) $C_{19}H_{34}O$ or $C_{18}H_{30}O_2$ (M^+), liq., IR $\nu^{liq.}$ 3400, 920 cm^{-1}, NMR δ^{CDCl_3} 0·88 (6H,d, $J = 5·6$), 0·89 (3H,s), 1·28 (6H,s), 5·04 (1H,dd, $J = 10·2$, 1·9), 5·20 (1H,dd, $J = 17$, 1·9), 5·93 (1H,dd, $J = 17$, 10·2). (*D*) $C_{15}H_{22}O$, liq., IR $\nu^{liq.}$ 3400, 1630, 880 cm^{-1}, NMR δ^{CDCl_3} 0·3–0·8 (2H,m), 1·02 (3H,s), 1·10 (3H,s), 1·23 (3H,s), 4·67–4·73 (2H,m). (*E*) $C_{10}H_{12}O_3$, liq., UV λ_{max}^{MeOH} 254 nm (ϵ 950), IR $\nu^{liq.}$ 1755, 1633 cm^{-1}, NMR δ^{CDCl_3} 1·23 (3H,s), 1·27 (3H,s), 1·55 (3H,s), 5·65 (1H,s).

Acknowledgements—Thanks are due to Professors M. Terasaka, Tokyo College of Pharmacy; H. Mitsuhashi, Hokkaido University; H. Hikino, Tohoku University; C. Djerassi, Stanford University, and P. R. Jefferies, and Drs. E. L. Ghisalberti, University of Western Australia and K. Sen, East India Pharmaceutical Work Ltd., for the authentic samples of spectral data.

Phytochemistry, 1971, Vol. 10, pp. 3331 to 3332. Pergamon Press. Printed in England.

SAURURECEAE

CONSTITUENTS OF *ANEMOPSIS CALIFORNICA**

LOHIT V. TUTUPALLI and MADHUKAR G. CHAUBAL
Pharmacognosy Division, School of Pharmacy, University of the Pacific, Stockton, Calif. 95207, U.S.A.

(*Received* 7 *June* 1971)

Abstract—Light petroleum extract of the roots and rhizomes of *Anemopsis californica* (Nutt.) Hook and Arn. yielded a compound identified as (+)-asarinin from its spectral and other analytical data.

ONLY TWO reports on the natural occurrance of (+)-asarinin are available.[1,2] Previously our laboratory reported on the chemical constituents of the essential oil from the roots and rhizomes of *Anemopsis californica.*[3,4] This paper is a part of the continuing study of the Saururaceae and reports the isolation and identification of (+)-asarinin from *A. californica.*

Of the powdered plant material 300 g[3,4] were extracted in a soxhlet with light petroleum. The crude crystals obtained from the concentrate were recrystallized from cyclohexane. (240 mg, 0·08% yield), m.p. 120–121° (capillary, uncorrected) and $[\alpha]_D^{20}$ +122°(*c* 0·1, $CHCl_3$). Mol. wt. 354 (Mass spectrum). (Found: C, 68·05; H, 4·68; O, 27·15; $C_{20}H_{18}O_6$ requires: C, 67·8; H, 5·1%.) UV: (nm) 236, 288; IR:(nm) 2853, 1501, 1442, 1375, 1365(sh), 1360, 1255, 1190–1180(doublet), 1074, 1035, 935. Mass: *m/e* 354 (parent peak), 203, 178,

* Part III in the series "Constituents of Anemopsis Californica".

[1] J. B. DENVERPORT and M. D. SUTHERLAND, *Australian J. Chem.* **1**, 384 (1954).
[2] K. HISAYUKI, K. SCHOICHI, O. AKIO and K. MUNIO, *Nippon Kagaku Zassi* **89**, 717 (1968).
[3] R. N. ACHARYA and M. G. CHAUBAL, *J. Pharm. Sci.* **57**, 1020 (1968).
[4] D. R. SANVORDEKAR and M. G. CHAUBAL, *J. Pharm. Sci.* **58**, 1213 (1969).