*7-Isopropyl-2, 9-dimethylphenanthrene and 2-Isopropyl-10-methylphenanthrene**

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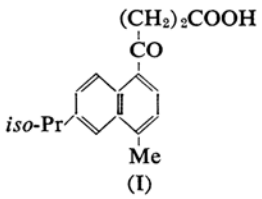
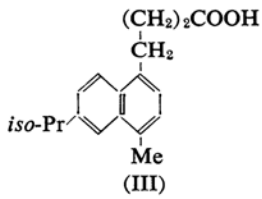
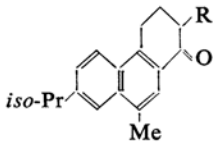
During degradative studies on the constitution of the conifer diterpene thunbergene[1], 7-isopropyl-2, 9-dimethylphenanthrene and 2-isopropyl-10-methylphenanthrene have been synthesized as reference compounds by standard methods.



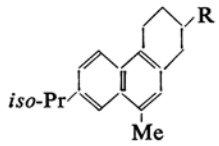
(I)



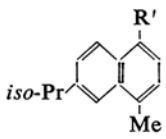
(III)



(IV) R, H
(V) R, Me



(VI) R, Me
(VII) R, H



(VIII) R', COOH
(IX) R', CH_2OH
(X) R', Me

The Friedel-Crafts succinoylation of 7-isopropyl-1-methylnaphthalene furnished 4-(6-isopropyl-4-methyl-1-naphthyl)-4-oxobutyric acid (I) along with a minor product, which was considered to be 4-(6-isopropyl-4-methyl-2-naphthyl)-4-oxobutyric acid (II) as mentioned below.

Reduction of the ketoacid (I) by the Wolff-Kishner method as modified by Huang-Minlon gave 4-(6-isopropyl-4-methyl-1-naphthyl)-butyric

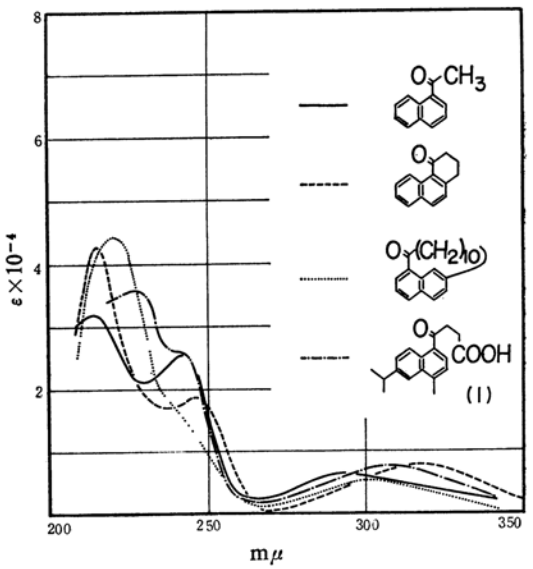


Fig. 1. UV Absorptions of α-naphthyl-keto systems in ethanol.

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1) H. Kobayashi and S. Akiyoshi, This Bulletin, 35, 1044 (1962).

acid (III), which was cyclized 1, 2, 3, 4-tetrahydro-7-isopropyl-9-methyl-1-oxophenanthrene (IV). Introduction of a methyl group at the 2-position of this cyclic ketone (IV) yielded 1, 2, 3, 4-tetrahydro-7-isopropyl-2, 9-dimethyl-1-oxophenanthrene (V). Wolf-Kishner reduction of the last ketone (V) yielded 1, 2, 3, 4-tetrahydro-7-isopropyl-2, 9-dimethylphenanthrene (VI) which furnished 7-isopropyl-2, 9-dimethylphenanthrene on dehydrogenation.

Similarly 2-isopropyl-10-methylphenanthrene was prepared from the cyclic ketone IV via VII.

In accordance with general principles[2], the succinoylation of 7-isopropyl-1-methylnaphthalene should occur at the 3- and 4-positions. This expectation was supported by the ultraviolet absorption spectra[3] which showed that one of the two isomeric naphthyl-oxobutyric acids I and II, had 1-naphthoyl chromophore (Fig. 1) while the other had 2-naphthoyl one (Fig. 3).

The structure of the 4-substituted product I was confirmed by obtaining 6-isopropyl-1, 4-dimethylnaphthalene (X)[4], via intermediates, VIII and IX. If the 5-substitution had occurred, instead, the reaction sequence should lead to 3-isopropyl-1, 5-dimethylnaphthalene[5].

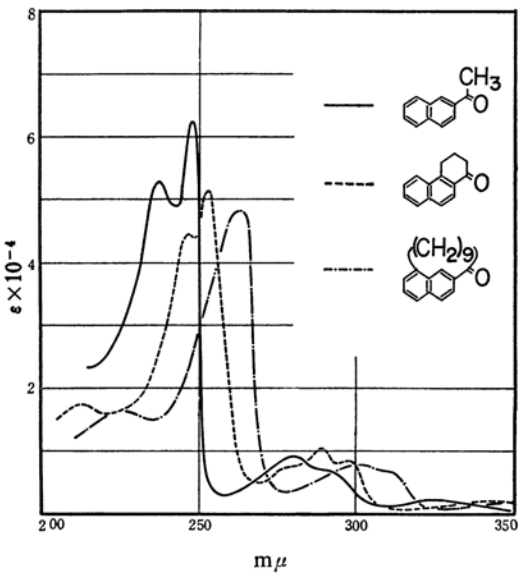

Fig. 2. UV Absorptions of 2-naphthoyl systems in ethanol.

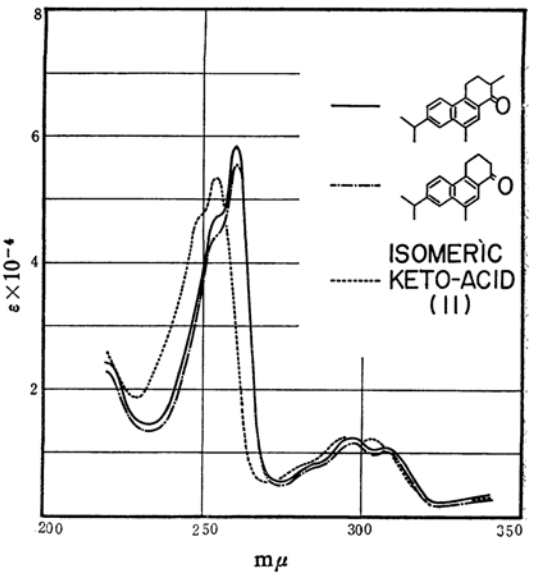

Fig. 3. UV Absorptions of the naphthoyl systems in this study.

Additional evidences for the assignments are that the cyclic ketones formulated as IV and V show similar ultraviolet spectra (Fig. 3) to those of the 2-naphthoyl system (Fig. 2)[3] and that final tricyclic hydrocarbons are phenanthrenes but not anthracenes. The 3-substituted naphthalene II has not been further investigated.

Experimental

Melting points are uncorrected and were measured on a Kofler micro hot stage. The ultraviolet spectra were recorded on a Hitachi EPS-2 type spectrophotometer. 7-Isopropyl-1-methylnaphthalene (eudalene) was synthesized according to the method of Ruzicka and Stoll[6] via 1,2,3,4-tetrahydro-7-isopropyl-1-oxonaphthalene[7]. The picrate, m. p. 92°C, was identical with that of eudalene prepared from eudesmol which occurred naturally. Pure eudalene was regenerated from the picrate by elution from alumina column.

7-Isopropyl-2, 9-dimethylphenanthrene. — Finely powdered aluminum chloride (28.0 g.) was added slowly to a stirred solution of eudalene (18.4 g.) and succinic anhydride (11.0 g.) in nitrobenzene (130 ml.) at 0°C, and after 30 hr. of a reaction period at room temperature the mixture was treated with ice (150 g.) and excess of hydrochloric acid (30 ml.). The removal of the nitrobenzene by steam-distillation furnished a resinous acid which was dissolved in 5% sodium carbonate and treated with activated charcoal. The resulting alkaline solution was acidified with dilute hydrochloric acid. A mixture of keto-acids (18.0 g.) was precipitated.

2) E. Berliner, "Organic Reactions", Vol. V, p. 229 (1949).
3) a) R. Huisgen and U. Rietz, *Ber.*, **90** 2768 (1957); b) R. Huisgen and U. Rietz, *Tetrahedron*, **2**, 271 (1958).
4) a) S. Dev, *J. Indian Chem. Soc.*, **33**, 561 (1956); b) L. Ruzicka, P. P. Th. Reichstein and L. Ehmann, *Helv. Chim. Acta*, **16**, 268 (1933).
5) A. S. Pfau and Pl. Plattner, *Helv. Chim. Acta*, **19**, 857 (1936).
6) L. Ruzicka and M. Stoll, ibid., **5**, 936 (1922).
7) E. Ochiai, T. Okamoto, M. Sekigawa, M. Nishikawa and K. Shono, *Pharm. Bull. (Tokyo)*, **5**, 48 (1957).

Repeated crystallization from ethanol gave 4-(6-isopropyl-4-methyl-1-naphthyl)-4-oxobutyric acid (I) (6.5 g.) as plates, m. p. 133.7~134.4°C.

Found: C, 75.85; H, 7.09. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%.

The mother liquor from this acid slowly deposited a crystalline acid (1.6 g.) which on repeated crystallization from ethanol gave the isomeric naphthyl-oxobutyric acid II (0.85 g.) m. p. 179.5~181.0°C.

Found: C, 75.77; H, 7.11. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%.

A mixture of 4-(6-isopropyl-4-methyl-1-naphthyl)-4-oxobutyric acid (I) (2.90 g.), 80% hydrazine hydrate (1.5 ml.), potassium hydroxide (2.0 g.) and diethylene glycol (15 ml.) was refluxed at 170~180°C for 2 hr., then excess of hydrazine and water were removed by distillation until the reaction temperature was 220°C and this temperature was maintained for an additional 3 hr. After acidification of the cooled reaction mixture, the product was purified by recrystallization from ethanol to give 4-(6-isopropyl-4-methyl-1-naphthyl)-butyric acid (III) as needles, m. p. 151.5~153.5°C (2.45 g.).

Found: C, 79.94; H, 8.18. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20%.

4-(6-Isopropyl-4-methyl-1-naphthyl)-butyric acid (III) (950 mg.) was added with stirring to a cooled 80% sulfuric acid (6.5 ml.) and then heated to 100°C for 1.5 hr. with occasional swirling. The cooled reaction mixture was added to ice and water and extracted with ether. The extract was washed with aqueous sodium carbonate, dried and evaporated to yield a crystalline solid IV which was purified by recrystallization from ethanol, m. p. 125.5~127.0°C, (750 mg.).

Found: C, 85.53; H, 8.02. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99%.

The semicarbazone formed white glittering plates decomposing at about 220°C. The crystals melted at 255°C with immediate decomposition upon rapid heating.

Found: C, 73.65; H, 7.59; N, 13.47, 13.45. Calcd. for $C_{18}H_{20}O \cdot CH_3N_3$: C, 73.75; H, 7.49; N, 13.58%.

Finely powdered sodium amide (250 mg.) suspended in dry benzene (10 ml.) was added to the cyclic ketone IV (1450 mg.) dissolved in dry benzene (5 ml.). After refluxing for 45 min., the evolution of ammonia ceased and a solid sodio-derivative separated. Addition of methyl iodide (1.0 g.) to the cooled solution resulted in an exothermic reaction, which was completed by refluxing for 30 min. The mixture was treated with dilute hydrochloric acid. Extraction with ether followed by crystallization from ethanol gave cycloketone V (650 mg.), m. p. 101~103°C.

Found: C, 85.69; H, 8.19. Calcd. for $C_{19}H_{22}O$: C, 85.67; H, 8.33%.

Semicarbazone could not be prepared in the usual way.

Reduction of the methylated cycloketone V (620 mg.) with 80% hydrazine hydrate (0.5 ml.), potassium hydroxide (500 mg.) and diethylene glycol (10 ml.) was carried out at 150°C for 2 hr., and then at 220°C for 4 hr. after removal of excess of hydrazine and water. The product VI was extracted with ether and then purified by elution with petroleum ether from an alumina column. A mixture of this tetrahydrophenanthrene VI (540 mg.) and 30% palladium on charcoal (50 mg.) was heated under reflux at 300°C for 2 hr. and then at 350°C for half an hour. The cooled mixture was extracted with petroleum ether and the crude product purified by chromatography from the same solvent on activated alumina, to give 7-isopropyl-1,9-dimethylphenanthrene which separated from ethanol in plates m. p. 77~79°C. λ_{max} (in hexane): 224, 250(shoulder), 257, 274, 281, 288, 299, 319, 328 and 355 mμ. log ε 4.44, 4.84, 5.00, 4.44, 4.37, 4.19, 4.08, 2.46, 2.40 and 2.45 respectively.

Found: C, 91.90; H, 8.19. Calcd. for $C_{19}H_{20}$: C, 91.88: H, 8.12%.

The picrate separated from ethanol in orange yellow needles melting at 133.5~134.5°C.

2-Isopropyl-10-methylphenanthrene.—The Wolff-Kishner reduction of 1,2,3,4-tetrahydro-7-isopropyl-9-methyl-1-oxophenanthrene (IV) (250 mg.) furnished 1,2,3,4-tetrahydro-7-isopropyl-9-methylphenanthrene (VII) (210 mg.), which could not be crystallized. Dehydrogenation of this tetrahydrophenanthrene with 30% palladium on charcoal as before furnished 2-isopropyl-10-methylphenanthrene, which separated from ethanol in white needles melting at 49.0~49.5°C. λ_{max} (in hexane): 223, 248(shoulder), 255, 272, 279, 285, 298, 318, 327 and 334 mμ.

log ε 4.37, 4.75, 4.88, 4.25, 4.21, 4.09, 4.01, 2.37, 2.35 and 2.38 respectively.

Found: C, 92.15; H, 7.75. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74%.

The picrate separated from ethanol as orange yellow needles melting at 123~124°C.

6-Isopropyl-1,4-dimethylnaphthalene via 6-Isopropyl-4-methyl-1-naphthoic Acid.—To a solution of sodium hypochlorite (30 ml. of 10% available chlorine) and sodium hydroxide (6 g.) in water (250 ml.) was dissolved 4-(6-isopropyl-4-methyl-1-naphthyl)-4-oxobutyric acid (I) in aqueous sodium hydroxide (20 ml. of 5%) and the mixture was heated at 65°C for 20 min. and then at 100°C under reflux for 20 min. The cooled solution was washed with ether and the aqueous solution was completely freed from ether by heating and then recooled. Acidification of this solution with sulfur dioxide furnished a solid which after recrystallization from benzene, gave 6-isopropyl-4-methyl-1-naphthoic acid (VIII) (470 mg.), m. p. 179.5~181.0°C.

Found: C, 79.05; H, 7.05. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%.

The naphthoic acid VIII (141 mg.) was methylated with diazomethane in ether. Excess of diazomethane was removed together with ether by evaporation. Residual oily methyl ester dissolved in dry ether was reduced with lithium alminum hydride (40 mg.). Excess of the hydride was decomposed by addition of dilute hydrochloric acid. Recrystallization from petroleum ether gave 1-hydroxymethyl-6-isopropyl-4-methylnaphthalene (IX) (129 mg.) m. p. 52.5~53.5°C.

Found: C, 83.99; H, 8.28. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47%.

The carbinol IX (129 mg.) and ethanol (120 mg.)

were dissolved together in liquid ammonia (3.5 ml.) and sodium (70 mg.) was added in small pieces with stirring[8]. A deep blue-colored mixture was obtained. Further ethanol was then added, and after the blue color had disappeared most of the ammonia was allowed to evaporate. The residue was cautiously decomposed by addition of dilute hydrochloric acid, and then extracted with ether. The ether extract was washed with water, and dried. Removal of the solvent followed by chromatography on an alumina column yielded 6-isopropyl-1,4-dimethylnaphthalene (62 mg.) which gave a picrate melting at 103.5~105°C (from ethanol). The mixed melting point of the picrate with that of the authentic sample[9] was undepressed and the infrared spectrum was superimposable on that of the authentic picrate.

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8) A. J. Birch, *J. Chem. Soc.*, **1945**, 809.

9) The author is indebted to Dr S. Dev for his kindly offering trinitrobenzene adduct of the authentic sample.