NOTES

Terpenoids. VII. The Isolation of Sandaracopimarinol from the Wood Oil of "Sugi"[*1]

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A recent investigation by Kondo, Imamura and Suda[1] showed the presence of isopimaric acid, sugiol, xanthoperol, ferruginol, β-sitosterol and a new diterpene alcohol, phyllocradanol, in the heartwood extractive of Sugi (*Cryptomeria japonica* D. Don.).

An acetone extract of the sawdust of Sugi wood gave an oil which afforded sandaracopimarinol[2] together with some of the compounds cited above. This is the first time sandaracopimarinol has been found in a natural source. Since sandaracopimaric acid[3] has already been found in the exudates of Sugi, the existence of sandaracopimarinol in the wood is of interest in view of a biogenetic pathway.

A diterpene hydrocarbon with a conjugated diene system was also isolated.

Experimental

The Isolation of an Oily Mixture.—Sawdust of Sugi (12 kg.) collected at a saw-mill on Mt. Seburi, near Fukuoka City, was extracted with hot acetone for 20 hr. The acetone was evaporated off, and the remaining oil was stirred into a tenfold volume of petroleum ether. The petroleum ether solution was then successively washed with a saturated aqueous sodium hydrogen carbonate, 5% sodium hydroxide, and water. After evaporation of the solvent from the solution, the volatile oil (6.35 g.) was removed by steam distillation. The residue was extracted with petroleum ether, which was evaporated off after drying over sodium sulfate, yielding a neutral material (36 g.). This substance was divided by simple distillation into three parts: fraction a, b. p. 110∼117°C/4 mmHg (5.5 g.); fraction b, b. p. 177∼185°C/4 mmHg (5.5 g.); and fraction c, residue (about 25 g.).

The Separation of Fraction b.—The fraction was chromatographed on an alumina column (100 g.). Petroleum ether eluted an oily diterpene hydrocarbon (1.88 g.) which gave a single peak on gas chromatograph.[*3]

Found: C, 88.04; H, 11.94. Calcd. for $C_{20}H_{32}$: C, 88.16; H, 11.84%.

n_D^{25} 1.5272, λ_{max} 241.5 mμ, ε 12300. ν_{max} 1628, 886 cm^{-1}.

A mixture of petroleum ether and ether (1 : 1) eluted a carbonyl compound (0.06 g.), and ether containing 1% methanol eluted an alcohol fraction (total: 3.40 g.), from which phyllocradanol (0.6 g., m. p. 187.5∼188.5°C, recrystallized from methanol) and sandaracopimarinol were isolated (see below).

The Separation of the Residue c.—The residue was chromatographed on another alumina column (190 g.). The results are shown in Table I.

TABLE I

Fr.	Solvent	Volume cc.	Yield g.
1	Petroleum ether	100	0.67
2	Petroleum ether	250	0.22
3	Petroleum ether+Ether (1%)	50	0.12
4	Ether	50	3.35
5	Ether	50	2.25
6	Ether	450	3.47
7	Ether+Methanol (1%)	300	0.82
8	Ether+Methanol (1%)	100	0.90
9	Ether+Methanol (5%)	150	3.59
10	Methanol	300	1.87

Fraction 1 was the same diterpene hydrocarbon that was obtained from fraction b. The presence of an ester was recognized in fractions 2 to 5. Ferruginol was separated from fraction 4 by further chromatography and was identified by infrared spectrum measurement.

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1) T. Kondo, H. Imamura and M. Suda, *Bull. Agr. Chem. Soc.*, **23**, 233 (1959); ibid., **24**, 65 (1960).

2) V. Galik, J. Kuthan and F. Petrů, *Chem. & Ind.*, **1960**, 722. Added in proof: The identity was later confirmed by direct comparion with authentic sample. The author thanks Professor F. Petrů for the identification.

3) S. Keimatsu, T. Ishiguro and G. Fukui, *J. Pharm. Japan* (*Yakugaku Zassi*), **57**, 69 (1937); J. W. Apsimon, B. Green and W. B. Whalley, *J. Chem. Soc.*, **1961**, 752; V. P. Arya, C. Enzell and H. Erdtman, *Acta Chem. Scand.*, **15**, 682 (1961); A. Tahara, O. Hoshino and N. Ikekawa, *Chem. Pharm. Bull.*, **10**, 995 (1962).

[*3] The author is indebted to Professor Yoshio Kitahara and Dr. Akira Yoshikoshi for the gas chromatography and elementary analysis of this hydrocarbon.

Fractions 6 to 9 contained mainly sandaracopimarinol and phyllocradanol. A crude sandaracopimarinol fraction (970 mg.) obtained from fraction 9 was treated with excess acetic anhydride and was left overnight.*4 A petroleum ether extract gave the residue (1.05 g.), which was chromatographed on an alumina column. Petroleum ether eluted the acetate of sandaracopimarinol (495 mg.), and ether eluted phyllocradanol (286 mg.). The saponification of the acetate with ethanolic potassium hydroxide afforded crude sandaracopimarinol (m. p. 40∼62°C). 3, 5-Dinitrobenzoate, m. p. 150.5∼151.5°C (from a petroleum ether - benzene mixture). Pure sandaracopimarinol, m. p. 63∼65°C, $[\alpha]_D -11°$ (c 2.34, chloroform), was obtained by the saponification of the 3, 5-dinitrobenzoate.

A crystalline ketone (m. p. 85°C, 0.03g.) was obtained from fraction 6. Fraction 10 solidified on standing and recrystallization from methanol afforded β-sitosterol (m. p. 136∼137°C, 435 mg.).

The Oxidation of Sandaracopimarinol.—The alcohol (530 mg.) in acetone (100 cc.) was oxidized with a Jones reagent[4] (about 3 cc.) in 30 min. The mixture was poured into water and extracted with ether. The crude acid (84 mg.) separated in the usual manner was recrystallized from acetone and was purified by silica gel chromatography to afford sandaracopimaric acid (m. p. 171∼175°C (from acetone)). No depression was observed by mixed melting point test with an authentic sample. The infrared spectra of the two samples were superimposable.

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*4 On the acetylation of the distilled diterpene alcohol fraction, most of the phyllocradanol was precipitated from the acetic anhydride solution.

[4] A. Bowers, T. G. Halsall and E. R. H. Jones, *J. Chem. Soc.*, **1953**, 2555.