Communications to the Editor

UDC 547.91 : 582.937

On the Presence of Ilexol Acetate in *Kopsia longiflora* MERRILL

In 1952, the writer isolated a new triterpene alcohol, ilexol,[1] from commercial bird-lime. It has also been found in the bark of *Ilex integra* THUNB.[2] and *I. crenata* THUNB.[3] as well as in the root of *Solidago altissima* LINNE[4] (0.7 g. of ilexol acetate was obtained from 2.7 kg. of dried roots),[5] showing that it is not specific to *Ilex* species.

In 1955, Crow and Michael[6] obtained an acetate, m.p. 279~281°(corr.); $[\alpha]_D$ 0°, of a triterpene alcohol, m.p. 203~204°, during studies on the alkaloids in the bark of *Kopsia longiflora* MERRILL (Apocynaceae). Mixed fusion of this alcohol and its acetate respectively with ilexol and its acetate showed them to be identical (cf. Table I).

TABLE I.

	m.p.(°C) (uncorr.)	$[\alpha]_D$
Ilexol	204~205°	−16.8°
mixed	202~204°	
Crow's alcohol	201~202°	−20.8°
Ilexol acetate	282~283°	
mixed	282~283°	
Crow's acetate	279~281°	

The infrared absorption spectra of all these samples also agreed well, thereby establishing the presence of ilexol acetate in the trunk bark of *Kopsia longiflora* MERRILL. Since Crow and Michael did not use any acids or alkalis, it is unlikely that ilexol acetate was formed from other compounds by isomerization.

Recently, Lahey[7] isolated a triterpene alcohol, bauerol, m.p. 216°(corr.), $[\alpha]_D$ −30°; acetate, m.p. 291~292°(corr.), $[\alpha]_D$ 0°, from *Acronychia baueri* SCHOTT. (Rutaceae). Mixed fusion of ilexol and its acetate respectively with bauerol and its acetate, performed by Prof. Lahey, did not show any depression. However, Prof. Lahey considers ilexol and bauerol to be not identical for the following reasons : (1) Negative rotation of ilexol acetate as compared to the rotation of ±0° for baueryl acetate,[8] and (2) the characteristic absorption in the ultraviolet region of all ilexol derivatives and absence of any bands in this region in the corresponding bauerol derivatives.

The writer expresses his deep gratitude to Dr. W. D. Crow of the Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia, for kind

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1) S. Iseda : Yakugaku Zasshi, **72**, 1064(1952).
2) S. Iseda, K. Yagishita, N. Toya : *Ibid.*, **74**, 422(1954).
3) K. Yagishita : Bull. Agr. Chem. Soc. Japan, **21**, 160(1957).
4) Private communication from Dr. T. Takemoto, Pharmaceutical Faculty, University of Osaka (March 3, 1957).
5) Unpublished data of the writer.
6) W. D. Crow, M. Michael : Australian J. Chem., 8, 129(1955).
7) Private communications from Prof. Lahey.
8) Dr. Crow also differs from the writer in the observation of the optical rotation of the alcohol acetate. Reëxamination of the optical activity of ilexol acetate by a Rudolph photoelectric polarimeter, performed by members of the Organic Chemistry Laboratory, Faculty of Science, Nagoya University, showed $[\alpha]_D$ −48.36°($c=0.053$, $l=4$ dm., $CHCl_3$). The writer is indebted to those who supplied optical data.

supply of the samples of the alcohol and its acetate from *Kopsia longiflora* and to Professor F. N. Lahey of Chemistry Department, University of Queensland, Brisbane, Australia, for carrying out the determation of a mixed melting point and for his keen discussions.

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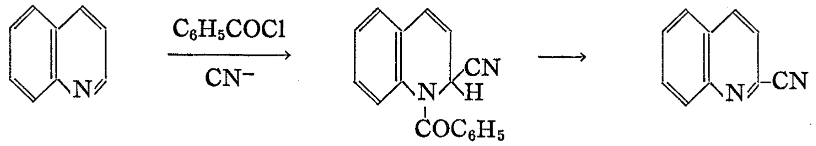
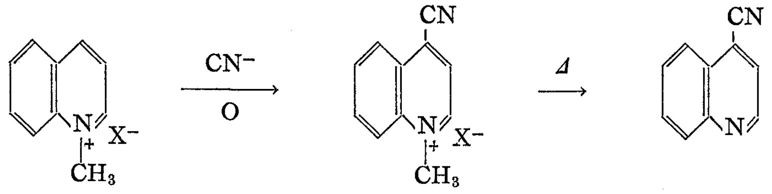
Synthesis of 2- and 4-Cyanopyridines

A method for direct introduction of cyano group at 2- or 4- position in pyridine ring includes the reactions reported by Reissert[1] and by Kaufmann.[2] These reactions gave good results with quinolines but generally did not proceed with pyridines.

Reissert :



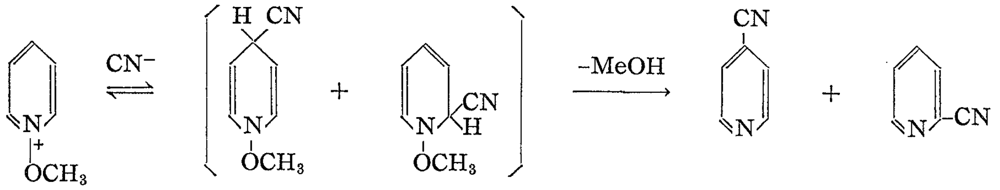
Kaufmann :



Pyridine and quinoline N-oxides easily form their quaternary salts. On considering the nucleophilic reactivity at 2- and 4-positions in the quaternary salts, a new method of directly introducing cyano group into pyridine rings was developed.

Pyridine or quinoline N-oxides were reacted with methyl iodide or dimethyl sulfate and to the solution of the resulting quaternary salts, potassium cyanide was added and stirred for about one hour at room temperature, by which the reaction was completed. The products, 2- and 4-cyanopyridines were extracted with chloroform and the isomers were separated by vacuum distillation or alumina chromatography. As the solvent for this reaction, water or water-dioxane mixture, and also other solvents are used. The reaction was completed at room temperature but higher temperature could also be used to advantage.

The possible mechanism of this reaction can be written as follows : The first step should be the attack by cyanide ion at 2- or 4-position of the pyridine ring and in the



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1) A. Reissert : Ber., **38**, 1603, 3415(1905).

2) A. Kaufmann, *et al.* : Ber., **42**, 3776(1909); **44**, 2058(1911); **45**, 1805(1912); **51**, 116(1918).