C-16 is eliminated to give conjugated diene (IXa). Existence of hydroxyl at C-20, another allylic position of 17:21 double bond, is excluded, since both ketone in deoxyleucotylindione are situated in six-membered ring [IR $\nu_{\max}$ cm^{-1} : 1701, 1690 (shoulder)].

Moreover, leucotylin showed intramolecular hydrogen bond between hydroxyls at C-16 and C-28 in its infrared spectrum (IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1} : 3676 (free hydroxyl), 3413, 3247 (bonded hydroxyls) in concentration of $10^{-4}M$). This phenomenon afforded further proof of the existence of hydroxyl at C-16, but not at C-15.

Therefore, leucotylin must have the structure represented as Ⅲa.

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A New Synthetic Method of Nucleosides

Recently, attention has been drawn to some of nucleosides and its derivatives for their physiological and biogenetic roles. Many workers have taken a part in the synthesis of the nucleosides and various methods[1~5] have been developed, however their scope is still limited. In this communication the authors intend to report a new synthetic procedure for natural and unnatural nucleosides, which is, in fact, a modification of Birkofer's method of N-acylation of heterocyclic bases, *via* their reactive trimethylsilyl derivatives.[6,7]

Trimethylsilyl derivatives of pyrimidines and purines were synthesized by usual method[8~10] and then applied for the preparation of several nucleosides by fusion with acylglycosyl halides. After condensation, the trimethylsilyl residue of Ⅲ could be removed by the treatment with aq. ethanol, to afford IV.

Quite recently, Birkofer, *et al.* reported that the reaction of tetrakis(trimethylsilyl)-uric acid with tribenzoylribofuranosyl bromide gave 3-ribofuranosyluric acid.[11]

Treatment of uracil with trimethylchlorosilane and triethylamine in benzene gave I in 72% yield, whose structure was confirmed by infrared spectrum. Further the fusion of Ⅱ with 2,3,5-O-tribenzoylribofuranosyl chloride[12] would produce 1-(2,3,5-tribenzoylribofuranosyl)trimethylsilyluracil (Ⅲ), which was treated with aq. ethanol to afford Ⅳ

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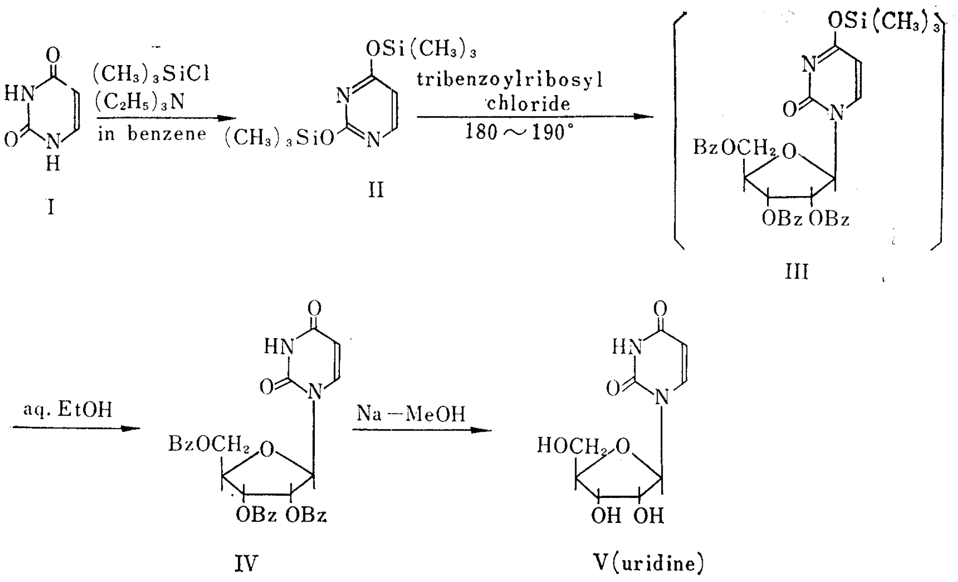

in 42% yield (based on uracil). The stage of reaction was determined by the thin layer chromatography. By following hydrolysis of IV, ribofuranosyluracil (V) (uridine) was obtained (yield 83% based on IV).

The strucures of nucleosides thus obtained (such as V) were cofirmed by ultraviolet[13,14] and infrared[15] spectra, moreover, from the results of nuclear magnetic resonance[16,17]

Table I. Physical Properties and Yields of the Trimethylsilylpyrimidines and Purines

Compound	b.p. (°C/mm. Hg)	m.p. (°C)	Yield (%)
Bis(trimethylsilyl)uracil	116/12	31~33	72
Bis(trimethylsilyl)thymine	124/14	63~65	89
Bis(trimethylsilyl)cytosine	168/30	122~123	69
Bis(trimethylsilyl)-N-acetylcytosine	137~139/6	62~68	71
Bis(trimethylsilyl)adenine	137/0.8	84~87	91
Bis(trimethylsilyl)-N-benzoyladenine	$177\sim183/8\times10^{-4}$	—	75
Bis(trimethylsilyl)hypoxanthine	135~142/0.8[a]	71~74	87
Tris(trimethylsilyl)guanine	167~168/1	—	88
Tris(trimethylsilyl)xanthine	163/1.5	87~90	77

a) Bath temperature

Table II. Physical Properties and Yields of the Synthetic Nucleosides

Compound	m.p. (°C)	$[\alpha]_D$	Yield (%)
1-β-D-Glucopyranosyluracil	204~206	+21.9 (H_2O)	28
1-β-D-Glucopyranosylthymine	269~271	+18.3 (H_2O)	43
1-(2,3,4,6-O-Tetracetyl-β-D-glucopyranosyl)-N-acetylcytosine	222~226	+43 ($CHCl_3$)	15
9-β-D-Glucopyranosyladenine	201~203	−8.5 (H_2O)	5.3
9-β-D-Glucopyranosylhypoxanthine	259~260	—	16
1-β-D-Ribofuranosyluracil (uridine)	165~166	+4.6 (H_2O)	35
1-β-D-Ribofuranosylthymine	180~181.5	−10.0 (H_2O)	46
9-(2,3,5-O-Triacetyl-β-D-ribofuranosyl)-hypoxanthine (Triacetylinosine)	238~240	—	12

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analysis, it was shown that all these substances possessed β-configurations in glycosidic centers.

The scope of reactions was investigated by applying several RNA and DNA bases, with glucosyl bromide and ribosyl chloride derivatives, the results of which are shown in Table I and II.

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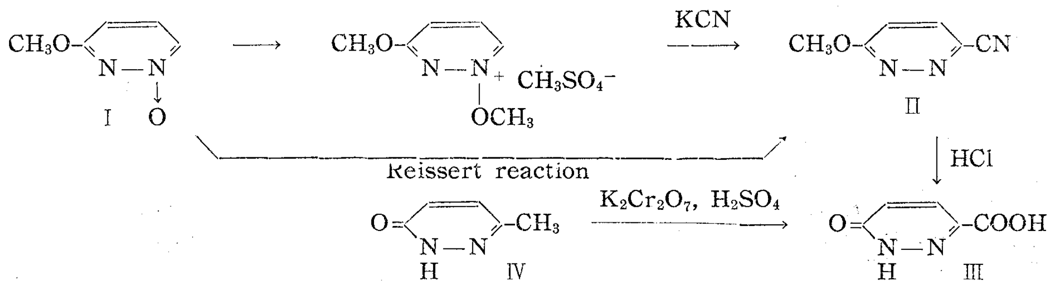
Pyridazinenitriles

Okamoto and Tani[1] reported the reactions of N-alkoxypyridinium derivatives with potassium cyanide, obtaining 2- and 4-cyanopyridines. The application of this reaction to pyridazines were successfully concluded. 3-Methoxypyridazine 1-oxide (I)[2] was treated with dimethylsulfate and so obtained methosulfate was reacted with potassium cyanide, affording 3-methoxy-monocyanopyridazine (II), m.p. 94° (*Anal.* Calcd. for $C_6H_5ON_3$: C, 53.33; H, 3.73. Found : C, 53.52; H, 4.03).

II was also obtained directly from I by Reissert reaction. Hydrolysis of II with conc. hydrochloric acid afforded a 6-hydroxy-3-pyridazinecarboxylic acid (III), m.p. 250° (decomp). Oxidation of 6-methyl-3-pyridazinol (IV) with potassium dichromate in sulfuric acid gave 6-hydroxy-3-pyridazinecarboxylic acid, m.p. 250° (decomp.),[3] undepressed on admixture with III, and infrared spectra of both compounds were identical.



From these results it is concluded that the cyano group was introduced in 6-position of I.

The reaction of other N-alkoxypyridazinium derivatives with potassium cyanide are now being investigated and details will be published in near future.

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[3] Uncorrected. M. Ogata, H. Kano reported m.p. 260°, This Bulletin, **11**, 29 (1963).