behavior in four different systems. Spectral data showed $\lambda_{max}^{H_2O}$ 259.5 mμ (ε 14,300). A mixture of this sample and dried 2′-deoxyadenosine[36] had m.p. 170–185°.

2,6,8-Trichloro-9-(3′,5′-di-O-acetyl-2′-deoxy-β-D-ribofuranosyl)purine. 2,6,8-Trichloropurine[20] (5.6 g., 0.025 mole) and 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose (II) (6.5 g., 0.025 mole) were fused *in vacuo* at 105° for 5 min. with chloroacetic acid (50 mg.). The melt was dissolved in ethyl acetate and was treated as in the preparation of 2,6-dichloro-9-(3′,5′-di-*O*-acetyl-2′-deoxy-α-D-ribofuranosyl)purine. The resulting semisolid was crystallized from absolute methanol to give 3.9 g. (37%) of pink crystals. Recrystallization of the product from absolute methanol gave 3.2 g. (30%) of 2,6,8-trichloro-9-(3′,5′-di-*O*-acetyl-2′-deoxy-β-D-ribofuranosyl)purine, m.p. 141–142°, $[\alpha]^{25}D$ −2.7° (*c* 1.02, EtOAc). Spectral data showed $\lambda_{max}^{pH\ 1}$ 278 and 246 mμ (ε 12,700 and 8050), $\lambda_{max}^{pH\ 11}$ 278 mμ (broad) (ε 15,200).

Anal. Calcd. for $C_{14}H_{13}Cl_3N_4O_5$: C, 39.7; H, 3.07; N, 13.2. Found: C, 39.5; H, 3.28; N, 13.2.

Acknowledgment. The authors wish to thank Dr. Christopher P. Whittle for his helpful discussions relative to this work.

The Synthesis of 1-(2′-Deoxy-α- and -β-D-ribofuranosyl)benzimidazoles Related to the Naturally Occurring Nucleosides of Vitamin B_{12}[1]

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Received March 6, 1965

Substituted 1-(2′-deoxy-α- and -β-D-ribofuranosyl)benzimidazoles have been prepared for the first time by a simple fusion of the requisite benzimidazole and 1,3,5-tri-O-acetyl-2-deoxy-D-ribofuranose in the presence of chloroacetic acid as a catalyst. The α- and β-anomers have been separated by fractional crystallization and column chromatography. Anomeric configuration has been assigned on the basis of p.m.r. spectra, and the nucleosides have been found to obey Hudson's rules of isorotation. The excellent yield of glycosides obtained by the present synthesis suggest the fusion procedure has wide application for the preparation of 2′-deoxy-D-ribofuranosyl nucleosides.

Renewed interest in the synthesis of benzimidazole ribonucleosides has been stimulated by the recent findings that 5,6-dimethyl-1-(α-D-ribofuranosyl)benzimidazole is incorporated into vitamin B_{12} in various microbiological systems, without cleavage of the nucleoside linkage.[3,4] The importance of vitamin B_{12} as a cofactor in many biochemical reactions is well established.[5–7] It has recently been demonstrated that vitamin B_{12} plays a significant role in the conversion of ribonucleotides to 2′-deoxyribonucleotides without glycosidic cleavage in the microorganism *L. leichmannii*.[8,9] Certain 1-(β-D-ribofuranosyl)benzimidazoles have been shown to exhibit antiviral activity.[10,11] It is quite possible that these compounds are simulating purine nucleoside analogs since the inhibition of influenza B virus by 5,6-dichloro-1-(β-D-ribofuranosyl)-benzimidazole (DRB) is reversed by adenosine.[12] It has been suggested that 5,6-dichloro-1-(β-D-ribofuranosyl)benzimidazole (DRB) interferes with preliminary synthesis of ribonucleic acid.[13] Recent work[14] has confirmed this suggestion and has shown DRB exhibits specific inhibition of chromosomal RNA synthesis. Evidence has recently been obtained for a benzimidazole nucleoside as a component of an enzyme isolated from wheat embryos.[15] Although biochemical interest in 2′-deoxy-D-ribofuranosylbenzimidazoles was expressed as early as 1956 by Tamm,[11] there is until the present work no report of their synthesis. Cooley and co-workers[16] in 1950 recognized the desirability of obtaining benzimidazole 2′-deoxynucleosides related to the naturally occurring purine 2′-deoxynucleosides. By using the silver salt of 5,6-dimethylbenzimidazole and 1-chloro-3,4-diacetyl-2-deoxy-D-ribopyranose, these authors obtained 5,6-dimethylbenzimidazole-1-

(1) Supported by Research Grants CA-04008-07 and CA-08109-01 from the National Cancer Institute of the National Institutes of Health, Public Health Service.
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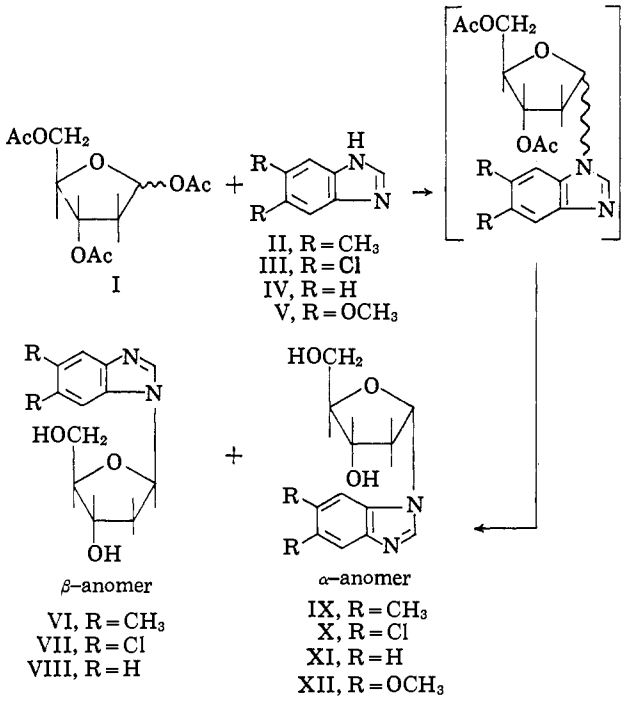
(2′-deoxy-D-ribopyranoside) of unassigned anomeric configuration. By a similar procedure an anomeric mixture of 1-(2′-deoxy-D-glucopyranosyl)-5,6-dimethylbenzimidazole was obtained which could not be crystallized or separated by fractionation procedures.[16] The goal of the present work was the synthesis of 1-(2′-deoxy-α- and -β-D-ribofuranosyl)benzimidazoles. The readily available 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose[17] (I) and the direct synthesis of various 2′-deoxy-D-ribofuranosylpurines[17] suggested the possibility of the preparation of the desired compounds *via* the fusion procedure.[18] When 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose (I) was fused at 160° with 5,6-dimethylbenzimidazole in the presence of a catalytic amount of chloroacetic acid and the reaction products were treated with alcoholic ammonia, 5,6-dimethyl-1-(2′-deoxy-D-ribofuranosyl)benzimidazole was obtained in 78% yield as an anomeric mixture of crystal-

Scheme I



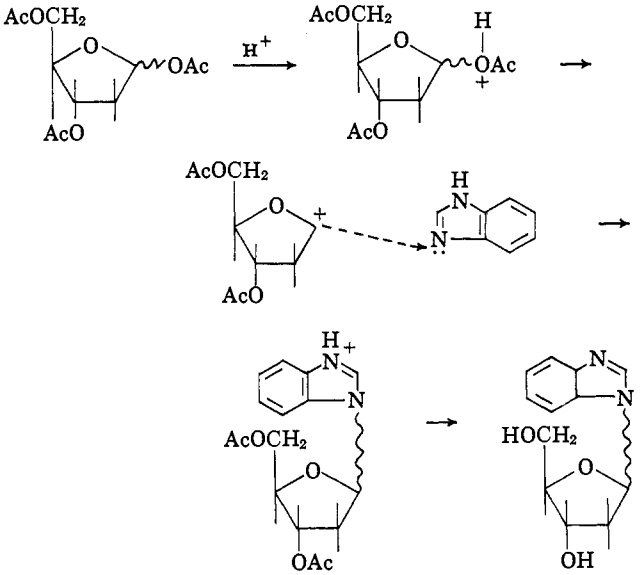
line nucleosides. The pure anomers 5,6-dimethyl-1-(2′-deoxy-α-D-ribofuranosyl)benzimidazole (IX) and 5,6-dimethyl-1-(2′-deoxy-β-D-ribofuranosyl)benzimidazole (VI) were separated by fractional crystallization and column chromatography. 5,6-Dichlorobenzimidazole (III), 5,6-dimethoxybenzimidazole[19] (V), and benzimidazole (IV) each fused readily with I to give a good yield of the corresponding crystalline glycosides after deacetylation (see Table I). 2-Chlorobenzimidazole and 2-benzimidazolone failed to yield nucleoside products. 5-Methoxybenzimidazole,[20] as might be expected, gave 1- and 3-glycosides of α- and β-anomers, a total of four different nucleosides whose separation could not be satisfactorily achieved. 4-Nitrobenzimidazole[21] gave some evidence (paper chromatography) of reacting with I, but the yield was extremely poor and no crystalline nucleoside was isolated. 2-Methylbenzimidazole and I fused to give greater than 80% yield of crystalline nucleoside material. Inspection of Table I shows that those benzimidazole derivatives

Table I

Compd.	pK_a	Yield of crystalline glycosides, % (α- and β-anomers)
Benzimidazole	5.52[a]	65
5,6-Dimethylbenzimidazole	5.99[a]	78
5,6-Dichlorobenzimidazole	4.74[a]	76
5,6-Dimethoxybenzimidazole	4.81[a]	79
5-Methoxybenzimidazole	5.72[a]	78
2-Methylbenzimidazole	6.10[a]	80
2-Chlorobenzimidazole	2.6[b]	None
2-Hydrobenzimidazole	2.4[b]	None
4-Nitrobenzimidazole	3.8,[c] 4.55[a]	Trace

[a] D. Rabiger and M. Joullie, *J. Org. Chem.*, **29**, 476 (1964), determined at 30 ± 0.5° in 5:95 ethanol–water. [b] L. S. Efros and B. A. Porai-Koshits, *Zh. Obsch. Khim.*, **23**, 697 (1953); *Chem. Abstr.*, **48**, 7604 (1954). [c] J. L. Rabinowitz and E. C. Wagner, *J. Am. Chem. Soc.*, **73**, 3030 (1951), determined in H_2O solution.

which are most basic (least acidic) (pK_a = 6.1–4.74) reacted most readily with 1,3,5-tri-*O*-acetyl-2′-deoxy-D-ribofuranose (I) in the fusion process. This would lend support to a reaction mechanism which involves alkylation of the benzimidazole nitrogen (tertiary nitrogen with the lone electron pair) by a 2-deoxy-D-ribofuranosyl-1-carbonium ion intermediate. The more basic benzimidazole derivative should be alkylated more readily.



Assignment of anomeric configuration to each reaction product was made on the basis of p.m.r. spectra.[17] Inspection of Table II reveals that for the α-anomer the $H_{1'}$ proton peak appeared as a multiplet of four with apparent $J_{H_{1'}}$ = 3.5–4.0 and ≈7 c.p.s. and a peak width of 10–11 c.p.s. (for example, see Figure 1). The β-anomer was characterized by a "pseudo-triplet" for the $H_{1'}$ proton peak with $J_{H_{1'}}$ ≈ 6.8 c.p.s. and a peak width of 13.5–14 c.p.s. (for

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Table II. Proton Magnetic Resonance Spectral Data for the $H_{1'}$ Proton and Optical Rotation of Certain 1-(2′-Deoxy-D-ribofuranosyl)benzimidazoles[a]

Nucleoside	M.p., °C.	Specific rotation $[\alpha]^{27}D$	P.m.r. patterns	α-Anomer $J_{H_1'}$, c.p.s.	α-Anomer Line width, c.p.s.	β-Anomer $J_{H_1'}$, c.p.s.	β-Anomer Line width, c.p.s.
1-(2′-Deoxy-β-D-ribofuranosyl)-benzimidazole (VIII)	153.5–154.5	−30.5	T			6.9	13.8
1-(2′-Deoxy-α-D-ribofuranosyl)-benzimidazole (XI)	181–182	+106.5	Q	3.8 7.1	10.9		
5,6-Dimethyl-1-(2′-deoxy-β-D-ribofuranosyl)benzimidazole (VI)	158–160	−32.2	T			6.0	13.8
5,6-Dimethyl-1-(2′-deoxy-α-D-ribofuranosyl)benzimidazole (IX)	225–226	+109.6	Q	4.0 7.1	11.1		
5,6-Dichloro-1-(2′-deoxy-β-D-ribofuranosyl)benzimidazole (VII)	168–169	−31.0	T			6.7	13.5
5,6-Dichloro-1-(2′-deoxy-α-D-ribofuranosyl)benzimidazole (X)	179.5–180	+107.5	Q	3.5 6.8	10.3		
5,6-Dimethoxy-1-(2′-deoxy-α-D-ribofuranosyl)benzimidazole (XII)	190–191	+109.6	Q	3.8 7.3	11.1		
2-Methyl-1-(2′-deoxy-β-D-ribofuranosyl)benzimidazole	206–207	+34.3	T			7.1	14.1

[a] All optical rotations were determined in methanol. All spectra were determined in dimethyl sulfoxide as a solvent with DDS as an internal standard using a Varian A-60 spectrometer. [b] T = "pseudo-triplet"; Q = multiplet of four.

example, see Figure 2). This difference in p.m.r. spectra has been found useful in the purine series[17] for anomeric assignment of the 2′-deoxyribofuranosides. Inspection of Table II shows that in each case where both anomers were isolated and purified, Hudson's isorotation rules[22] are found to apply. The more

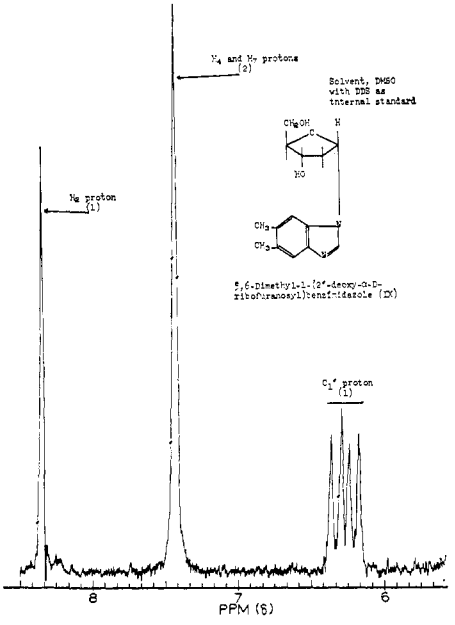

Figure 1.

dextrorotatory of the anomeric pair has the α-D-configuration. All nucleosides prepared in this study were found to be chromatographically homogeneous in at least four systems. The ultraviolet absorption spectral data for the 1-(2′-deoxy-D-ribofuranosyl)-benzimidazoles are listed in Table III. As might be expected there was essentially no difference detected in the ultraviolet absorption between anomeric pairs.

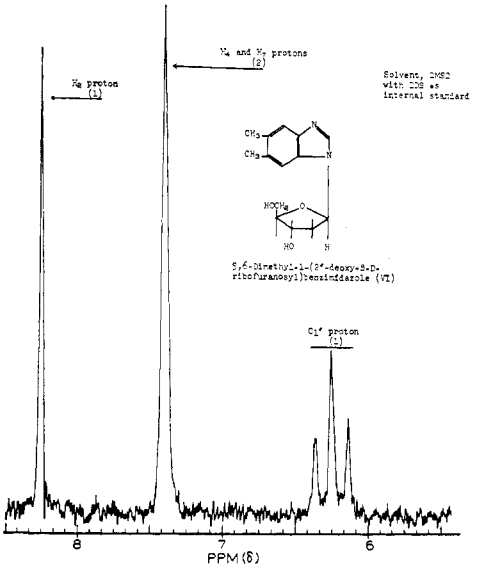

Figure 2.

Experimental Section

5,6-Dimethyl-1-(2′-deoxy-D-ribofuranosyl)benzimidazoles (IX and VI). A mixture of 5,6-dimethylbenzimidazole[23] (1.46 g., 0.01 mole) and 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose[17] (2.60 g., 0.01 mole) was fused at 160° (oil bath temperature). After 5 min. a clear melt was obtained and chloroacetic acid (0.05 g.) was added and the mixture heated under reduced pressure (2–3 cm.) for 15 min. The cold reaction mixture was dissolved in benzene (50 ml.) and a small

(22) C. S. Hudson, *J. Am. Chem. Soc.*, 31, 66 (1909).

(23) Purchased from Aldrich Chemical Co., Milwaukee, Wis.

Table III. Ultraviolet Spectra of 1-(2′-Deoxy-D-ribofuranosyl)benzimidazoles[a]

Subst. 1-(2′-deoxy-D-ribofuranosyl)-benzimidazole	MeOH λ_{max}	MeOH ϵ	pH 11 λ_{max}	pH 11 ϵ	pH 1 λ_{max}	pH 1 ϵ
5,6-Dimethyl-	249	7500	249	7300	255 s	4800
	279	5200	278	5300	271 s	6600
	282	5200	288	5200	277	8200
	289	5400			285	7900
5,6-Dichloro-	254	6900	253	6970	246	5400
	281 s	4400	281 s	4310	277.5 s	5300
	287	5830	287	5600	284	7600
	296	5980	295	5530	293	7500
5,6-Dimethoxy-	244	5000				
	249	5570	248.5	5960		
	255 s	4560	257 s	4930		
	292	8750	291	8030	292.5	11300
	296 s	8430	299 s	7710	301	9940
	300	7470				
None	246	6830	246	6650	249	4510
	251 s	6550	250 s	6370	262	4850
	265	3380	265	3440	268.5	6200
	273	4070	272.5	3950	275	5750
	281	4080	280	3720		
2-Methyl-	245	7120	245	7650	242.5	5340
	266	3280	266 s	4350	262.5 s	5580
	274	3430	273	5280	269	7530
	281	5280	280	5590	276	8010

[a] s = shoulder.

amount of insoluble material (0.05 g.) was removed by filtration. Benzene was removed from the filtrate and the remaining sirup was treated with 100 ml. of methanolic ammonia (methanol saturated at 0°) and allowed to stand at room temperature for 24 hr. After the methanolic ammonia had been removed, the residue (3.0 g.) solidified. The gummy solid was triturated with a small amount of ethanol, and the colorless crystalline solid was collected and recrystallized from methanol to give fine white needles of 5,6-dimethyl-1-(2′-deoxy-α-D-ribofuranosyl)benzimidazole (IX) (0.7 g.), m.p. 225–226°.

Anal. Calcd. for $C_{14}H_{15}N_2O_3$: C, 64.1; H, 6.9; N, 10.7. Found: C, 64.2; H, 7.1; N, 10.4.

The combined filtrates were placed on a column of alumina (1.5 × 6 in.) in ethanol and eluted with ethanol (2000 ml.) and water (1000 ml.). The ethanol eluent contained 0.4 g. of the α-anomer. The material eluted with water was recrystallized from water to obtain an additional 0.33 g. of the α-anomer. Evaporation of the mother liquors from this recrystallization gave an oil which solidified on standing. This material was recrystallized from ethanol–ethyl acetate to give 5,6-dimethyl-1-(2′-deoxy-β-D-ribofuranosyl)benzimidazole (VI) (0.7 g.), m.p. 158–160°.

Anal. Calcd. for $C_{14}H_{18}N_2O_3$: C, 64.1; H, 6.9; N, 10.7. Found: C, 63.9; H, 6.7; N, 11.0.

The total yield of nucleosides was 1.73 g., 64.9%. This reaction was repeated using 5.8 g. of 5,6-dimethylbenzimidazole and 13.0 g. of 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose to obtain a total yield of crystalline nucleosides (mixture of anomers) of 78%.

5,6-Dichloro-1-(2′-deoxy-D-ribofuranosyl)benzimidazoles (VII and X). A mixture of 5,6-dichlorobenzimidazole[23] (1.88 g., 0.01 mole) and 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose[17] (2.6 g., 0.01 mole) was fused to a clear melt at 160°. Chloracetic acid (0.02 g.) was added and heating was continued *in vacuo* for 15 min. The cold reaction mixture was treated with benzene (50 ml.) to precipitate a small amount (0.10 g.) of insoluble material. The benzene filtrate was evaporated to obtain a sirup which was dissolved in methanol saturated with ammonia (100 ml.) and allowed to stand at room temperature for 24 hr. The methanol was then removed and the residue (4.05 g.) solidified. The crude product was dissolved in a minimum amount of ethanol, placed on a column of alumina (14 × 5 cm.) in ethanol, and eluted with ethanol (750 ml.) and ethanol–water (500 ml., 1:1). Both eluents yielded a mixture of products, m.p. 137.5–154° (1.80 g., 59%). When 7.5 g. of 5,6-dichlorobenzimidazole and 13.0 g. of 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose were fused under similar conditions, the yield of anomeric material was 76%. The anomeric mixture (9.6 g.) was separated by fractional crystallization from ethyl acetate to yield the more insoluble 5,6-dichloro-1-(2′-deoxy-α-D-ribofuranosyl)benzimidazole (X) (3.3 g.), m.p. 179.5–180°.

Anal. Calcd. for $C_{12}H_{12}N_2O_3Cl_2$: C, 47.5; H, 4.0; N, 9.2; Cl, 23.4. Found: C, 47.6; H, 4.0; N, 9.1; Cl, 23.2.

The more soluble 5,6-dichloro-1-(2′-deoxy-β-D-ribofuranosyl)benzimidazole (VII) was isolated in 2.1-g. yield, m.p. 168–169°.

Anal. Calcd. for $C_{12}H_{12}N_2O_3Cl_2$: C, 47.5; H, 4.0; N, 9.2; Cl, 23.4. Found: C, 47.8; H, 4.3; N, 9.1; Cl, 23.1.

1-(2′-Deoxy-D-ribofuranosyl)benzimidazoles (VIII and XI). A mixture of benzimidazole[23] (4.7 g., 0.04 mole) and 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose (I) (13.0 g., 0.05 mole) was fused at 160°. After 3 min., a clear melt was obtained and chloroacetic acid (0.15 g.) was added. The mixture was heated under reduced pressure (2–3 cm.) for an additional 20 min. The cooled reaction mixture was dissolved in benzene (200 ml.) and filtered; the filtrate was evaporated to a clear, glassy sirup. The sirup was dissolved in methanol saturated with ammonia (250 ml.) and allowed to stand at room temperature for 48 hr. The methanol was evaporated from the reaction mixture and the semicrystalline residue was triturated with warm ethanol, cooled, and filtered to yield crude 1-(2′-deoxy-α-D-ribofuranosyl)benzimidazole (XI) (2.6 g.), m.p. 176–179°. The product was recrystallized from ethanol–ethyl acetate to obtain colorless needles, m.p. 181–182°. *Anal.* Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.52; H, 6.0; N, 12.0. Found: C, 61.4; H, 6.1; N, 12.2.

All filtrates from the isolation of the α-anomer (XI) were combined, dissolved in ethanol, and placed on a column of alumina (4.5 × 21 cm.). The first 100 ml. of eluent contained acetamide, m.p. 80–82°. The following 800 ml. of ethanol contained glycoside product (3.5 g.), m.p. 135–142°. This material was fractionally recrystallized from ethanol–ethyl acetate mixtures to obtain an additional 0.8 g. of the α-anomer (XI) and 0.6 g. of 1-(2′-deoxy-β-D-ribofuranosyl)-benzimidazole (VIII), m.p. 153.5–154.5°.

Anal. Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.5; H, 6.0; N, 12.0. Found: C, 61.4; H, 6.1; N, 12.2.

2-Methyl-1-(2'-deoxy-β-D-ribofuranosyl)benzimidazole. A mixture of 2-methylbenzimidazole[24] (4.88 g., 0.04 mole) and 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose[17] (13.0 g., 0.05 mole) was fused at 160° to obtain a clear melt after 4 min. Chloracetic acid (0.15 g.) was added and the mixture was heated for 20 min. *in vacuo*. The cold reaction mixture was dissolved in benzene (200 ml.) and filtered to remove 0.065 g. of insoluble material. The filtrate was evaporated to a clear sirup, treated with methanol saturated with ammonia (250 ml.), and allowed to stand at room temperature for 48 hr. Methanol was removed from the mixture and the residue partially crystallized on trituration with ethanol. The solid was collected by filtration and recrystallized from ethanol to obtain 2-methyl-1-(2'-deoxy-β-D-ribofuranosyl)benzimidazole (2.29 g.) as a colorless, crystalline compound, m.p. 206–207°.

Anal. Calcd. for $C_{13}H_{16}N_2O_3$: C, 62.9; H, 6.5; N, 11.3. Found: C, 62.9; H, 6.5; N, 11.4.

After isolation of the β-anomer, the combined filtrates were dissolved in ethanol and placed on a column of alumina (4.5 × 21 cm.). The column was eluted with ethanol and 25-ml. fractions were collected. The fractions (3–5) contained glycoside (5.07 g.) together with a little acetamide which was removed by sublimation at 50° (0.1 mm.). Recrystallization of the crude glycoside mixture provided an additional 0.7 g. of the pure β-anomer, but the α-anomer could not be separated from the β-anomer successfully by fractional crystallization. The total yield of crystalline anomeric nucleosides was 7.36. g. (80%).

5,6-Dimethoxy-1-(2'-deoxy-α-D-ribofuranosyl)benzimidazole (XII). A mixture of 5,6-dimethoxybenzimidazole[19] (3.56 g., 0.02 mole) and 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose[17] (6.0 g., 0.023 mole) was fused to a clear melt at 160° (bath temperature). Chloracetic acid (0.01 g.) was added and the mixture was heated *in vacuo* for 20 min., until rapid evolution of acetic acid had ceased. The mixture was cooled and treated with benzene as usual; the benzene filtrate was evaporated to dryness. The residual sirup was treated with methanol saturated with ammonia (150 ml.) and allowed to stand at room temperature for 24 hr. The methanol was removed and remaining sirup was treated with ethanol–ether and scratched with a glass rod to obtain a crystalline product (4.66 g., 79%, m.p. 153.5–165°). This crude glycoside was fractionally recrystallized from methanol–ethyl acetate to obtain 5,6-dimethoxy-1-(2'-deoxy-α-D-ribofuranosyl)benzimidazole (XII) (0.8 g.) as colorless needles, m.p. 190–191°.

Anal. Calcd. for $C_{14}H_{18}N_2O_5$: C, 57.1; H, 6.2; N, 9.5. Found: C, 57.4; H, 6.4; N, 9.6.

The mother liquors after isolation of pure XII yielded material, m.p. 162.5–172.5°. This material, however, could not be obtained free of contaminating α-anomer by fractional crystallization.

(24) K. Hofmann, "Imidazole and Derivatives," Interscience Publishers, New York, N. Y., 1953, p. 381.

10,22-Dioxokopsane, N_a-Methyl-10,22-dioxokopsane, and N_a-Carbomethoxy-10,22-dioxokopsane. Three New Alkaloids of *Pleiocarpa mutica* Benth.[1]

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Careful chromatography of the extract of the stem bark of Pleiocarpa mutica Benth. yielded three weakly basic dihydroindole alkaloids. On the basis of spectral data, mainly conventional and high-resolution mass spectrometry, they were shown to be 10,22-dioxokopsane (IC), its N_a-methyl and N_a-carbomethoxy derivatives IB and IA, respectively. These structural assignments were confirmed by direct chemical correlation of IA with IC and IB and conversion of the latter to pleiocarpinilam, an alkaloid of known structure.

In continuation of the investigation[2,3] of the minor alkaloids from the stem bark of *Pleiocarpa mutica* Benth., we have isolated three additional new weakly basic alkaloids A, B, and C by very careful repeated chromatography of the crude extract on alumina and silica gel.

The similarity of their mass spectra, which exhibited an analogous pattern and molecular weights of 378, 334, and 320, suggested that all three alkaloids contain the same carbon skeleton. The high-resolution mass spectrum revealed the elemental composition to be $C_{22}H_{22}N_2O_4$, $C_{21}H_{22}N_2O_2$, and $C_{20}H_{20}N_2O_2$, respectively, differences which suggest that alkaloid A contains a carbomethoxy group and alkaloid B a methyl group more than alkaloid C. As a typical example the spectrum of B is shown in Figure 1 in the form of a conventional, low-resolution spectrum,[4] and in Figure 2

(1) Part XXXII of the series Application of Mass Spectrometry to Structure Problems. For part XXXI see ref. 2.

(2) H. Achenbach and K. Biemann, *Tetrahedron Letters*, in press.

(3) H. Achenbach and K. Biemann, *J. Am. Chem. Soc.*, 87, 4177 (1965).

(4) Figure 1 represents a computer-compiled presentation of the high-resolution spectrum (Figure 2), by summing the abundance of all species of the same nominal mass and plotting these summed intensities *vs.* that of the most abundant ion.[5] Because of its high intensity, the largest peak (the molecular ion) is displayed as one-half its relative size. The resulting "bar graph" has the appearance of conventional mass spectra. It is practically identical with the spectrum obtained with a single-focusing mass spectrometer (CEC 21-103C) except that that instru-