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SYNTHESIS OF IMIDAZOLINE-2-THIONES AND IMIDAZOLIDINE-2-THIONES

J. FERNÁNDEZ-BOLAÑOS, F. GARCÍA GONZÁLEZ, J. GASCH GÓMEZ and M. MENÉNDEZ GALLEGO
Instituto de Química "Alonso Barba" del C.S.I.C. Facultad de Ciencias de la Universidad de Sevilla, Spain

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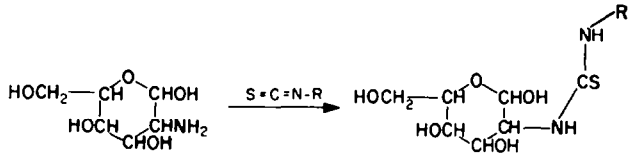
Abstract—1-Aryl (or alkyl)-4,5-(D-glucopyrano)imidazolidine-2-thiones are obtained by condensation of 2-amino-2-deoxy-D-glucose with aryl (or alkyl) isothiocyanates. 1-Aryl-4-D-*arabino*tetrahydroxybutylimidazoline-2-thiones are prepared by reaction of N-arylamino-1-deoxy-D-fructoses with potassium thiocyanate. A comparative structure study of both types of compound is reported.

THE application of D-glucosamine hydrochloride in the synthesis of imidazole-2-thiols was initiated by Neuberg and Wolff,[1] who proposed the structure of 1-aryl or alkyl-2-thiol-4-D-*arabino*tetrahydroxybutylimidazole for the compounds obtained by reaction of this aminosugar with phenyl and allyl isothiocyanates. Later, Pauly and Ludwig[2] and Ishifuku[3] formulated the structure of 2-thiol-4(5)-D-*arabino*-tetrahydroxybutylimidazole for the condensation product of D-glucosamine hydrochloride with potassium thiocyanate.



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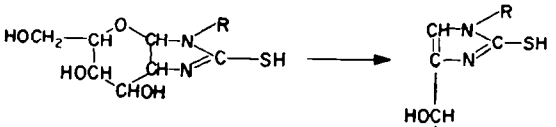

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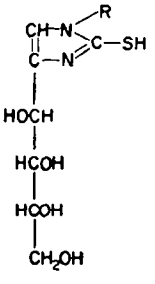


IV

[1] C. Neuberg and H. Wolff, *Ber. Dtsch. Chem. Ges.* **34**, 3840 (1901).
[2] H. Pauly and E. Ludwig, *Ztsch. f. Physiol. Ch.* **121**, 170 (1922).
[3] K. Ishifuku, *J. Pharm. Soc., Japan* **48**, 584 (1928).

Earlier papers on this subject,[4,5] described several new condensation products of D-glucosamine with aryl or alkylisothiocyanates formulated as 2-thiolimidazole derivatives (IV), in accordance with the compounds mentioned earlier and also with the mechanism proposed[4] for this type of reaction.

Later the structure of these compounds and their application to the synthesis of imidazolecarboxaldehyde derivatives was studied. With this in mind, the SH group of the condensation product of D-glucosamine hydrochloride with potassium thiocyanate was removed by the use of Raney nickel,[6,7] and also protected by alkylation.[6,8,9] The tetrahydroxybutyl side chain was proved by periodic acid evaluation, and oxidized into a formyl group with sodium metaperiodate. Therefore, these results support the structure of 2-thiol-4(5)-D-arabinotetrahydroxybutylimidazole (IV, R = H) formulated by Pauly and Ludwig.[3]

At the same time the elucidation of the structure of the condensation products of D-glucosamine with isothiocyanates was undertaken by similar methods. In 1951 we reported[10] that the compound obtained by reaction of D-glucosamine with phenylisothiocyanate (IV, R = C_6H_5) was desulphurized with Raney nickel and then oxidized by periodic acid, giving an oxygen consumption in accordance with only two adjacent hydroxyl groups and not with a tetrahydroxybutyl chain. This result may be explained by a formula of pyranoimidazolidine similar to III. Further support for this structure was obtained by the isolation of triacetyl derivatives[10] of several of these condensation products, and by the studies carried out in the Physical Laboratories of the University of Seville using X-ray crystallographic methods.[11]

Finally, and also supported by the work of Ettlinger[12] who considers that the potentially enolic heterosubstituted thioamides exist mainly in the thione form, the structure 1-aryl(or alkyl)-4,5-(D-glucopyrano)imidazolidine-2-thiones (V) was proposed[10,13–15] for the products obtained by reaction of D-glucosamine with

[4] F. García González and J. Fernández-Bolaños, *Anales Real Soc. Españ. Fís. y Quím.* **44B,** 233 (1948).

[5] F. García González and J. Fernández-Bolaños, *Anales Real Soc. Españ. Fís. y Quím.* **45B,** 1527 (1949).

[6] F. García González and J. Fernández-Bolaños, *Anales Real Soc. Espa. Fisñ. y Quím.* **45B,** 1531 (1949).

[7] J. Fernández-Bolaños, J. Ruiz Cruz y F. García González, *Anales Real Soc. Españ. Fís. y Quím.* **46B,** 501 (1950).

[8] J. Fernández-Bolaños, J. Ruíz Cruz and F. García González, *Anales Real Soc. Españ. Fís. y Quím.* **47B,** 737 (1951).

[9] A. Paneque Guerrero, F. García González y J. Fernández-Bolaños, *Anales Ins. Farm. Españ.* 309 (1956).

[10] F. García González, J. Fernández-Bolaños y J. Ruíz Cruz, *Anales Real Soc. Españ. Fís. y Quím.* **47B,** 299 (1951).

[11] M. Cubero, L. Roldán and A. Pérez Puente, *Anales Real Soc. Españ. Fís. y Quím.* **53A,** 126 (1957); L. Brú and M. Pérez Rodríguez, *Ibid.* 53A, 149 (1957); *Ibid.* 54A, 31 (1958); L. Brú, M. Cubero and L. Roldán, *Ibid.* 53A, 155 (1957); P. Muñoz González, *Anales de la Univ. Hispalense* (Sevilla, Spain), **20,** 47 (1960).

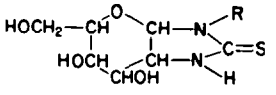
[12] M. G. Ettlinger, *J. Amer. Chem. Soc.* **72,** 4699 (1950).

[13] F. García González, J. Fernández-Bolaños and A. Paneque Guerrero, *Las Ciencias* (Madrid, Spain) **29,** 189 (1959).

[14] F. García González, J. Fernández-Bolaños and A. Paneque Guerrero, *Anales Real Soc. Españ. Fís. y Quím.* **57B,** 379 (1961).

[15] XXVI *Congress Luso-Espanhol para o Progresso das Ciencias* Vol II. p. 343. Porto, Portugal, June (1962).

TABLE 1

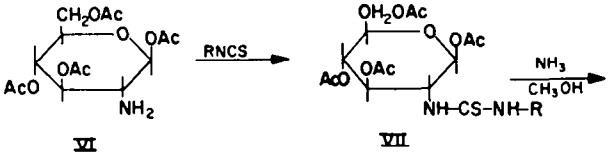


V

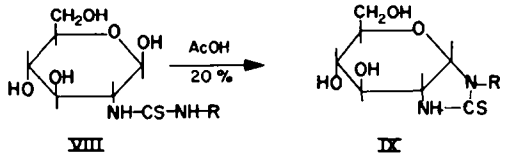
1-Aryl (alkyl)-4,5(D-glucopyrano)imidazolidine-2-thiones

R	M.p.
Ethoxycarbonylmethyl	168–169°
m-Tolyl	151–155°
p-Tolyl	234–236° dec
o-Nitrophenyl	184°
m-Nitrophenyl	132–135°
5-Nitro-o-tolyl	189–190°
p-Bromophenyl	232–234°
α-Naphtyl	232–233°
β-Naphtyl	226–227°

isothiocyanates. In the Table 1 all the compounds previously reported[4,5,13,14] are included. Recently, Morel[16] described the synthesis of several compounds with the same structure(V), starting from 1,3,4,6,tetra-O-acetyl-2-amino-2-deoxy-β-D-glucopyranose[17] according with the following reactions:



VI VII



VIII IX

Also Huber[18] has reported the synthesis of 1-aryl (or alkyl) -2-thiol-4-D-*arabino*-tetrahydroxybutylimidazoles by the reaction of N-aryl (alkyl)amino-1-deoxy-D-fructoses with ammonium thiocyanate in the presence of acetic acid, the structure of these compounds (IV) being the same as formulated in our earlier papers.[1,4]

In order to compare both types of compounds, the condensation products of D-glucosamine with *p*-tolyl, *p*-methoxyphenyl and *p*-ethoxyphenylisothiocyanates were prepared and in addition the reaction compounds of N-*p*-tolyl, N-*p*-methoxyphenyl and *p*-ethoxyphenylamino-1-deoxy-*D*-fructoses with potassium thiocyanate were obtained. The analysis, melting points and rotatory powers of these substances, recorded in the Tables 2 and 3,[15] prove that they are isomeric.

[16] Ch. J. Morel, *Helv. Chim. Acta* **44**, 403 (1961).
[17] M. Bergmann and L. Zervas, *Ber. Dtsch. Chem. Ges.* **64**, 975 (1931).
[18] G. Huber, O. Schier and J. Druey, *Helv. Chim. Acta* **43**, 713 (1960); *Ibid.* **43**, 1787 (1960).

TABLE 2. 1-ARYL (ALKYL)-4,5(D-GLUCOPYRANO)IMIDAZOLIDINE-2-THIONES (V)

R	Molecular formula	M.p.	$(\alpha)_D^{17°}$ C_5H_5N	Analysis							
				Found %				Required %			
				C	H	N	S	C	H	N	S
p-Tolyl*	$C_{14}H_{18}O_4N_2S$	245° dec.	+64° *c*, 0·9	54·5	5·8	9·0	10·7	54·2	5·8	9·0	10·3
p-Methoxyphenyl†	$C_{14}H_{18}O_5N_2S$	225° dec.	+74° *c*, 2·1	51·3	5·8	8·8		51·5	5·6	8·6	
p-Ethoxyphenyl	$C_{15}H_{20}O_5N_2S$	232–233°	+52° *c*, 0·9	52·6	5·7	8·3	9·3	52·9	5·9	8·2	9·4

* cf.[16]: m.p. 237–238°. $[\alpha]_D$ +79·5 (dimethyl formamide); † cf.[16]: m.p. 235–236°, $[\alpha]_D$ +79·6° (dimethyl formamide).

TABLE 3. 1-ARYL-4-D-ARABINOTETRAHYDROXYBUTYLIMIDAZOLINE-2-THIONES

R	Molecular formula	M.p.	$[\alpha]_D^{17°}$ C_5H_5N	Analysis							
				Found %				Required %			
				C	H	N	S	C	H	N	S
p-Tolyl*	$C_{14}H_{18}O_4N_2S$	215–216°	−30° *c*, 2·0	54·1	5·6	9·0	10·3	54·2	5·8	9·0	10·3
p-Methoxyphenyl	$C_{14}H_{18}O_5N_2S$	215–216°	−21° *c*, 1·6	51·8	5·7	8·7	9·5	51·5	5·6	8·6	9·8
p-Ethoxyphenyl†	$C_{15}H_{20}O_5N_2S$	223° dec.	−20° *c*, 0·7	53·1	5·8	8·5	9·3	52·9	5·9	8·2	9·4

* cf.[18]: m.p. 205–207°, $[\alpha]_D$ −33° (pyridine); † cf.[18]: 214–215°.

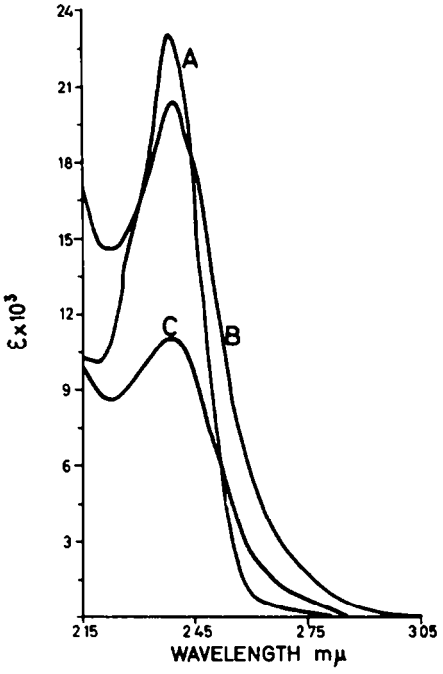


FIG. 1

(A) 1-Allyl-4,5-(D-glucopyrano)imidazolidine-2-thione.
(B) 1-Phenyl-4,5-(D-glucopyrano)imidazolidine-2-thione.
(C) 1-*p*-Tolyl-4,5-(D-glucopyrano)imidazolidene-2-thione.

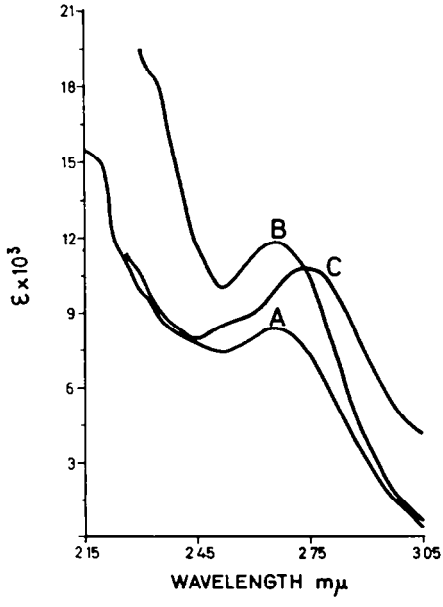
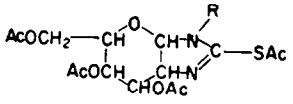


FIG. 2

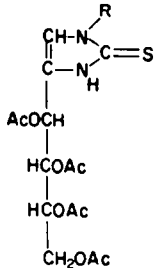
(A) 1-*p*-Tolyl-4-D-*arabino*tetrahydroxybutylimidazoline-2-thione.
(B) 1-*p*-Ethoxyphenyl-4-D-*arabino*tetrahydroxybutylimidazoline-2-thione.
(C) 1-*p*-Tolyl-4-D-*arabino*tetra-O-acetylhydroxybutylimidazoline-2-thione.

The UV spectra of both types are in accordance with the structures proposed for them. The imidazolidine-2-thione shows an absorption maximum at 240 mμ.[19] The imidazol-2-thiols have a characteristic wavelength absorption at ca. 260 mμ, which Lawson and Merley[20] consider mainly due to contributions from the thione form. The absorption of the S-alkyl derivatives occurs at a slightly lower wavelength and with a much reduced intensity.[20] The condensation products of D-glucosamine with aryl (or alkyl)isothiocyanates show strong absorption at 238 mμ (Fig. 1) in accordance with an imidazolidine-2-thione structure. The 4(5)-D-*arabino*tetrahydroxybutyl-imidazoline-2-thione and the 2-benzylthio derivative have (Fig. 3) the characteristic maximum at 256 mμ (ε, 24,000) and at 253 mμ (ε 9,000). The reaction compounds of N-arylamino-D-*iso*glucosamine with potassium thiocyanate (Fig. 2, curves A, B) show absorption typical of imidazoline-2-thiones in the region of 260 mμ. The corresponding S-benzyl derivatives, listed in Table 4, give curves with a slight maximum or inflection at a slightly lower wavelength (Fig. 4).

The acetyl derivatives of both types prepared by reaction with acetic anhydride and pyridine show analyses, melting points and rotatory powers, Tables 5 and 6, in agreement with the formulae X and XI of tetraacetates proposed for them. Morel[16] considers the acetyl derivatives (X) as tetraacetates of a tetra (or di?) hydroimidazoles.



X



XI

The UV and IR spectra support this view. The carbonyl frequency of the thiol esters is considered[21] to be 40–60 cm^{-1} lower than the normal esters. The acetyl derivatives, listed in Table 5, (X, R = *p*-$CH_3C_6H_4$, *p*-C_2H_5O C_6H_4) show a strong absorption at 5·96 μ and 5·86 μ, assigned to the —CO—S group, in addition to the carbonyl acetate absorption at 5·75 μ and 5·67 μ. On the other hand the acetyl derivatives, Table 6 (XI, R = *p*-$CH_3C_6H_4$, *p*-$C_2H_5OC_6H_4$) show no absorption of the thiol esters. The structure of imidazoline-2-thiones for these products (XI) is also supported by the fact that the UV spectrum of the tetraacetyl derivative of 1-*p*-tolyl-4-D-*arabino*tetrahydroxybutylimidazoline-2-thione (Fig. 2, curve C) is similar to those mentioned above (Fig. 2, curves A, B). Also, the compounds XI, R = *p*-$CH_3C_6H_4$, *p*-$C_2H_5OC_6H_4$, show absorption at 2·90 (N—H monomeric) and at 3·16, 3·18 (N—H associated). In relation to the compounds X, R = *p*-$CH_3C_6H_4$, *p*-$C_2H_5OC_6H_4$, we have found that they do not show the characteristic N—H bond absorption.

[19] H. Behringer and H. Meier, *Liebigs Ann.* **607**, 67 (1957).
[20] A. Lawson and H. V. Merley, *J. Chem. Soc.* 1103 (1956).
[21] A. W. Baker and G. H. Harris, *J. Amer. Chem. Soc.* **82**, 1923 (1960).

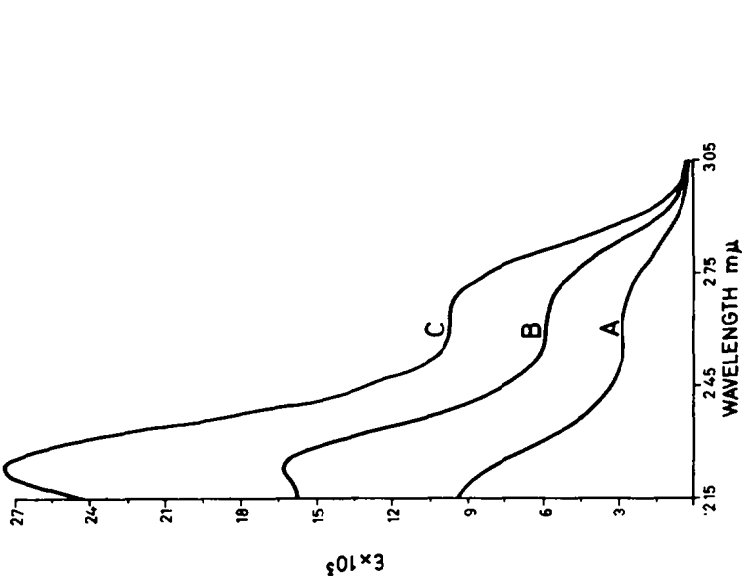


FIG. 4

(A) 1-*p*-Tolyl-2-benzylthio-4-D-*arabino*tetrahydroxybutylimidazole.
(B) 1-*p*-Methoxyphenyl-2-benzylthio-4-D-*arabino*tetrahydroxybutylimidazole.
(C) 1-*p*-Ethoxyphenyl-2-benzylthio-4-D-*arabino*tetrahydroxybutylimidazole.

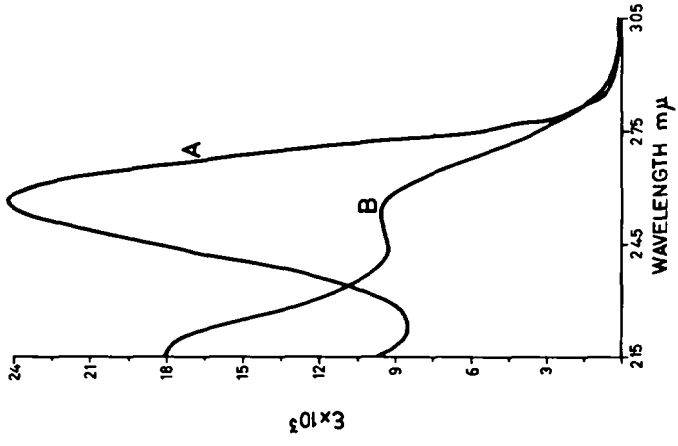


FIG. 3

(A) 4(5)-D-*Arabino*tetrahydroxybutylimidazoline-2-thione.
(B) 2-Benzylthio-4(5)-D-*arabino*tetrahydroxybutylimidazole.

TABLE 4. 1-ARYL-2-BENZYLTHIO-4-D-ARABINOTETRAHYDROXYBUTYLIMIDAZOLES

R	Molecular formula	M.p.	$[\alpha]_D$ C_5H_5N	Analysis							
				Found %				Required			
				C	H	N	S	C	H	N	S
p-Tolyl	$C_{21}H_{24}O_4N_2S$	157–158°	−25° *c*, 1·0	63·2	6·4	7·1	7·9	63·0	6·0	7·0	8·0
p-Methoxyphenyl	$C_{21}H_{24}O_5N_2S$	127·5–128·5°	−26° *c*, 0·6	60·7	5·7	6·8	7·8	60·6	5·8	6·7	7·7
p-Ethoxyphenyl	$C_{22}H_{26}O_5N_2S$	127·5–141°	−21° *c*, 1·0	61·3	6·2	6·5	7·4	61·4	6·1	5·7	7·4

TABLE 5. 1-ARYL-2-ACETYLTHIO-4,5(3,4,6-TRI-O-ACETYL-D-GLUCOPYRANO)IMIDAZOLINES

R	Molecular formula	M.p.	$[\alpha]_D^{27°}$ C_5H_5N	Analysis							
				Found %				Required %			
				C	H	N	S	C	H	N	S
p-Tolyl	$C_{22}H_{26}O_8N_2S$	197–199°	+62° *c*, 1·5	55·2	5·4	6·2	6·9	55·2	5·5	5·8	6·7
p-Methoxyphenyl	$C_{22}H_{26}O_9N_2S$	171·5–173·5°	+76° *c*, 1·0	52·9	5·2	5·9	7·4	53·4	5·3	5·7	6·5
p-Ethoxyphenyl	$C_{23}H_{28}O_9N_2S$	179·5–180·5°	+61° *c*, 0·5	54·3	5·4	5·1	6·5	54·3	5·6	5·5	6·3

TABLE 6. 1-ARYL-4-D-ARABINOTETRA-O-ACETYLHYDROXYBUTYLIMIDAZOLINE-2-THIONE

R	Molecular formula	M.p.	$[\alpha]_D^{27°}$ C_5H_5N	Analysis							
				Found %				Required %			
				C	H	N	S	C	H	N	S
p-Tolyl	$C_{22}H_{26}O_8N_2S$	79·5–80·5°	−120° *c*, 0·9	55·6	5·7	6·1	6·5	55·2	5·5	5·8	6·7
p-Methoxyphenyl	$C_{22}H_{26}O_9N_2S$	107–109°	−104° *c*, 0·2	53·4	5·6	5·5	6·5	53·4	5·3	5·7	6·5
p-Ethoxyphenyl	$C_{23}H_{28}O_9N_2S$	148–150°	−120° *c*, 1·1	54·4	5·4	5·6	6·6	54·3	5·6	5·5	6·3

EXPERIMENTAL

1-*Aryl*-4,5-(D-*glucopyrano*)*imidazolidine*-2-*thiones* (Table 2). To a solution of 2-amino-2-deoxy-D-glucose hydrochloride (0·2 mole) in water (400 ml), containing Na_2CO_3(0·1 mole), arylisothiocyanate (0·2 mole) was added, and the mixture made homogeneous with acetone. After 4 days at room temp the solvent was removed (red. press.) by heating on a water bath. The residue was washed with water and filtered. Yields after one crystallization from ethanol, 2·5–8%.

1-*Aryl*-4-D-*arabinotetrahydroxybutylimidazoline*-2-*thione* (Table 3). A solution of N-arylamino-1-deoxy-D-fructose[22] (0·1 mole) in 1N HCl (10 ml) with KSCN (0·1 mole) was heated on a boiling water bath for 10–25 min until crystallization occurred. The compound was filtered and washed with water, yield 10%. Samples for analysis were crystallized 3 times from ethanol–water (1:1).

1-*Aryl*-2-*benzylthio*-4-D-*arabinotetrahydroxybutylimidazoles* (Table 4). A mixture of 1-aryl-4-D-arabinotetrahydroxybutylimidazoline-2-thione (0·1 mole), benzylchloride (0·1 mole) and $NaHCO_3$ (0·1 mole) in 90% ethanol (150 ml) was boiled under reflux for 1 hr. The solvent was removed under red. press. by heating on a water bath. The residue was washed with water and filtered, yield 90%. Samples for analysis were recrystallized 3 times from ethanol-water (1:1).

1-*Aryl*-2-*acetylthio*-4,5-(3,4,6-*tri*-O-*acetyl*-D-*glucopyrano*)*imidazolines* (Table 5). To a solution of 1-aryl-4,5-(D-glucopyrano)imidazolidine-2-thione (1 g) in pyridine (10 ml), acetic anhydride (10 ml) was added. The mixture was allowed to stand 1 day at room temp and was then poured into water (100 ml). The acetate crystallized after a few minutes. Samples for analysis were recrystallized twice from ethanol.

1-*Aryl*-4-D-*arabinotetra*-O-*acetylhydroxybutylimidazoline*-2-*thiones* (Table 6). 1-Aryl-4-D-*arabino*-tetrahydroxybutylimidazoline-2-thione (1 g) was dissolved in pyridine (10 ml) and acetic anhydride (10 ml) added. The solution was allowed to stand 1 day at room temp and poured into water (100 ml). After some hours this was decanted from the gummy solid, which was again allowed to stand in water. Samples for analysis were recrystallized 3 times from a mixture of benzene and pet. ether.

UV spectra were made on a Beckman G 2400 Spectrophotometer. IR spectra were recorded on a Beckman IR-5A Infra-red Spectrophotometer. Rotations were determined with a Bippich Zeiss-Winkel polarimeter.

1-Allyl-4,5-(D-glucopyrano)imidazolidine-2-thione,[4] m.p. 143–144°, $[\alpha]_D^{22°}$ +18° (*c*, 1 pyridine). UV: Fig. 1, λ_{max} 238 mμ (ε, 23,000). (Found: C, 46·0; H, 6·0; N, 10·9; S, 12·6. Calc. for $C_{10}H_{16}O_4N_2S$: C, 46·4; H, 6·2; N, 10·8; S, 12·3%)

1-Phenyl-4,5-(D-glucopyrano)imidazolidine-2-thione,[4] m.p. 209–211° dec, $[\alpha]_D^{22°}$ +58° (*c*, 1 pyridine). UV: Fig. 1, λ_{max} 238 mμ (ε 20,000). (Found: C, 52,4; H, 5·1; N, 9·2; S, 10·6. Calc. for $C_{13}H_{16}O_4N_2S$: C, 52·7; H, 5·4; N, 9·4; S, 10·8%).

1-*p*-Tolyl-4,5-(D-glucopyrano)imidazolidine-2-thione (Table 2), UV: Fig. 1, λ_{max} 238 mμ (ε, 11,000).

4(5)-D-*arabino*tetrahydroxybutylimidazoline-2-thione,[3-4] m.p. 207° dec, $[\alpha]_D^{22}$ −15° (*c*, 1 water). UV: Fig. 3, λ_{max} 259 mμ (ε, 24,000). (Found: C, 38·5; H, 5·3; N, 12·7; S, 14·3. Calc. for $C_7H_{12}O_4N_2S$: C, 38·2; H, 5·5; N, 12·7; S, 14·6%).

1-*p*-Tolyl-4-D-*arabino*tetrahydroxybutylimidazoline-2-thione (Table 3), UV: Fig. 2, λ_{max} 265 mμ (ε, 8,500).

1-*p*-Ethoxyphenyl-4-D-*arabino*tetrahydroxybutylimidazoline-2-thione (Table 3), UV: Fig. 2, λ_{max} 267 mμ (ε, 12,000).

2-Benzylthio-4(5)-D-*arabino*tetrahydroxybutylimidazole,[6] m.p. 163–165°, UV: Fig. 3, λ_{max} 253 mμ (ε, 9,500). (Found: C, 54·0; H, 5·8; N, 8·9; S, 9·9. Calc. for $C_{14}H_{18}O_4N_2S$: C, 54·2; H, 5·8; N, 9·0; S, 10·3%).

1-*p*-Tolyl-2-benzylthio-4-D-*arabino*tetrahydroxybutylimidazole (Table 4), UV: Fig. 4, λ_{max} 260 mμ (ε, 2,850).

1-*p*-Methoxyphenyl-2-benzylthio-4-D-*arabino*tetrahydroxybutylimidazole (Table 4), UV: Fig. 4, λ_{max} 259 mμ (ε, 6,000).

1-*p*-Ethoxyphenyl-2-benzylthio-4-D-*arabino*tetrahydroxybutylimidazole (Table 4), UV: Fig. 4, λ_{max} 255 mμ (ε, 10,000).

1-*p*-Tolyl-2-acetylthio-4,5-(3,4,5-tri-O-acetyl-D-glucopyrano)imidazoline (Table 5), IR: λ_{max}^{Nujol} 5·75 μ (—CO—), 5·96 μ (—CO—S—).

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1-*p*-Ethoxyphenyl-2-acetylthio-4,5-(3,4,6-tri-O-acetyl-D-glucopyrano)imidazoline (Table 5), IR: $\lambda_{max}^{CHCl_3}$ 5·67 μ (—CO—), 5·86 μ (—CO—S—), single beam operation.

1-*p*-Tolyl-4-D-*arabino*tetra-O-acetylhydroxybutylimidazoline-2-thione (Table 6), UV: Fig. 3, λ_{max}^{EtOH} 274 mμ (ε, 11,000). IR: $\lambda_{max}^{CHCl_3}$ 2·90 μ, (N–H monomeric), 3·16 μ (N–H associated), 5·69 μ (—CO—).

1-*p*-Ethoxyphenyl-4-D-*arabino*tetra-O-acetylhydroxybutylimidazoline-2-thione (Table 6), IR: $\lambda_{max}^{CHCl_3}$ 2·90 μ (N–H monomeric), 3·18 μ (N–H associated), 5·70 μ (—CO—).

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