Tetrahedron Letters No. 6, 10-12, 1960. Pergamon Press Ltd. Printed in Great Britain.

NITROGEN GLYCOSIDES. N-GLUCOSYL DERIVATIVES OF SUBSTITUTED RHODANINES

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(Received 8 February 1960)

GLUCOSYL derivatives of rhodanine and substitutes rhodanines have not been reported in the Literature. These compounds appear to be of significance both from the physiological and chemical points of view. It is generally known that several compounds containing the thiazoline, thiazolidine, or thiazolidine-thione(2)-one(4), i.e. rhodanine ring are physiologically active; the bacteriostatic, fungistatic and other pharmacological and toxicological activities of the rhodanine derivatives have been investigated recently.[1] Chemically, the chief interest lies in the tautomerism of the rhodanine ring: if it forms glycosyl derivatives what is the exact structure

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[1] F.C. Brown et al., J. Amer. Chem. Soc. 78, 384 (1956); W.M.McLamore et al., Ibid. 75, 105 (1953); M. Janewiec et al., Bull. Acad. Pol. Sci. Cl. VI, 5, 201 (1957). W. Wieniawski et al., Roczn. Chem. 32, 545 (1958); C.R. Bradsher and F.C. Brown, Nature, Lond. 168, 17 (1951) J. Amer. Chem. Soc. 76, 114 (1954); G.J.M. van der Kerk et al., Mededel. Landbouwhogeschool Gent 18, 402 (1953); Chem. Abstr. 48, 316 (1953); S.A. Tavab and A. Mustafa et al., Nature, Lond. 183, 607 (1959); F.J. Allan, G.G. Allan and C.F.M. McNeil, Nature, Lond. 184, 1637 (1959).

of these compounds?

We have found that rhodanine derivatives containing exocyclic double bend in position 5 give crystalline tetraacetyl-glucosyl-derivatives with acetobromo-glucose in aqueous acetone in the presence of sodium hydroxide.

We have prepared the following compounds in this way:

N-(tetraacetyl-D-glucosyl)-5-benzalrhodanine (I), bright yellow needles from methanol (yield 57%); m.p. 193 - 194°; $[\alpha]_D^{20} = -171^\circ$ (c=1, in Py), U.V. spectrum, λ_{max} in mμ (log ε): 280 (4.02); 374 (4.46). (Found C, 51.8; H, 4.7; N, 2.4; S, 11.3; acetyl, 29.9%; Calc. for $C_{22}H_{25}O_{10}NS_2$ C, 52.3; H, 4.6; N, 2.5; S, 11.6; acetyl, 31.1%.)

N-(tetraacetyl-D-glucosyl)-5-anisalrhodanine (II), bright yellow needles from chloroform-methanol, and from acetone. (Yield 56%) m.p. 226 - 228°. $[\alpha]_D^{20} = -181^\circ$ (c=1, in Py); U.V. spectrum, λ_{max} in mμ (log ε γ: 245 (3.89), 295 (4.17), 391 (4.65). (Found: N, 2.6; Calc. for $C_{26}H_{27}O_{11}NS_2$; N, 2.4%).

N-(tetraacetyl-D-glucosyl)-5-isopropylidene rhodanine (III), pale yellow needles from methanol (yield: 40%); m.p.: 193 - 195°; $[\alpha]_D^{20} = -99^\circ$ (c=1, in Py). U.V. spectrum: λ_{max} in mμ, (log ε): 270 (3.92); 345 (4.44). Found: C, 47.3; H, 5.0; N, 3.0; S, 12.9; acetyl, 34.9; (Calc. for $C_{20}H_{25}O_{10}NS_2$: C, 47.7; H, 5.0; N, 2.8; S, 12.7; acetyl, 34.2%)

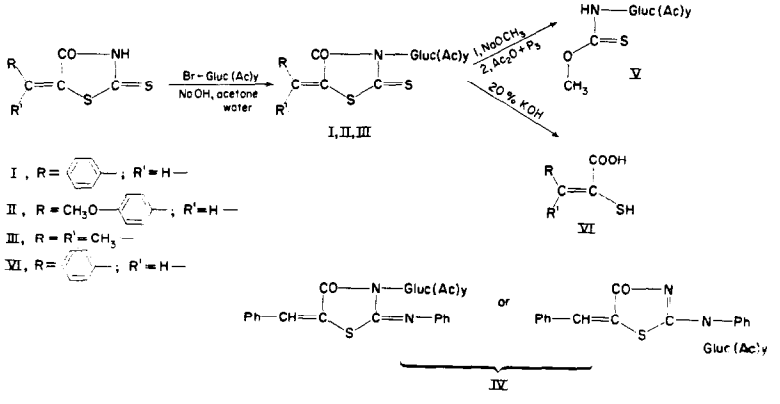
N-(tetraacetyl-D-glucosyl)-5-benzal-2-phenylamine-thiazolidene-(4) (IV), yellow needles from methanol-water, (yield 42%). m.p.: 203 - 204°; $[\alpha]_D^{20} = -76^\circ$ (c=1, in Py) U.V. spectrum λ_{max} in mμ (log ε): 230 (4.19); 336 4.34). (Found: C, 59.1; H, 5.1; N, 4.6; S, 5.1; acetyl, 28.0; Calc. for $C_{30}H_{30}O_{10}N_2S$: C, 59.0; H, 5.0; N, 4.6; S, 5.3; acetyl, 28.2%).

The following experiments and degradation products prove the structure of (I), (II) and (III). We have ascertained the intact thione group in the

tetraacetyl-glucosyl-derivatives; the N-alkyl-rhodanines did not react with acetobromo-glucose; β-phenyl-α-thiel-acrylic acid (V) was formed from (I) by alkaline degradation with 10% potassium hydroxide; our conclusive proof that these compounds are N-glycosyl derivatives: by methanolysis of (I) and (II) with sodium methylate in abs. methanol followed by acetylation of the amorphous product we have obtained N-(tetraacetyl-D-glucosyl)-methylcarbamate (VI), which was identified with an authentic[2] sample.

It is to be noted that the reaction of rhodanine and acetobromo-glucose in aqueous acetone in the presence of sodium hydroxide gave only (III) and no glucosyl derivative of the unsubstituted rhodanine could be obtained in this way.

The structure of (IV) has not yet been proved. In our opinion, of the possible tautomeric forms there are two N-glucosyl structures which ought to be taken into consideration.[3]



[2] A. Müller and A. Wilhelms, Ber. 74, 698 (1941).

[3] F.B. Dains et al., Univ. Kansas Sci. Bull. 24, 15 (1936), Chem. Abstr. 32, 3396 (1936).