Carbohydrate Research, 100 (1982) C31–C32
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

Preliminary communication

Reduction products and bromodeoxy derivatives of dehydro-L-ascorbic acid 2-phenylhydrazone

BERNARD GROSS†, MOHAMED ALI EL SEKILY*, and SOHILA MANCY*

Laboratoire de Chimie Organique III, Université de Nancy I, Case Officielle 140, 54037 Nancy Cedex (France)

(Received December 2nd, 1981; accepted for publication, December 14th, 1981)

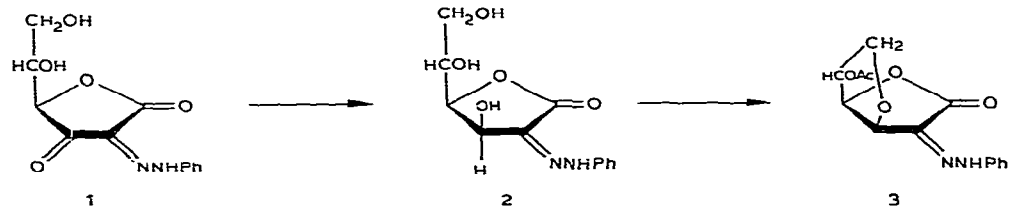
Dehydro-L-ascorbic acid 2-phenylhydrazone (L-*threo*-2,3-hexodiulosono-1,4-lactone 2-phenylhydrazone)[1,2] (**1**) is a compound of great synthetic potential; it reacts with aryl- and aroyl-hydrazones, giving mixed bishydrazones[3–5], and with hydroxylamine, to give the 3-oxime 2-phenylhydrazone[3]. From a different viewpoint, compound **1** has been considered a useful, synthetic precursor to nitrogen heterocycles[3,4,6]. In this respect, we describe the reduction, and also some bromodeoxy derivatives, of **1**.

On treatment of dehydro-L-ascorbic acid 2-phenylhydrazone (**1**) with sodium borohydride in methanol solution at −10° a product (m.p. 156–157°) was obtained whose elemental analysis, and n.m.r.- and mass-spectral data, agreed with the molecular formula $C_{12}H_{14}N_2O_5$, and, accordingly, it was given the structure L-*xylo*-2-hexulosono-1,4-lactone 2-phenylhydrazone (**2**). The infrared spectrum of **2** showed a hydroxyl band at 3450 cm^{-1} and the lactone band at 1750 cm^{-1}, but the carbonyl absorption (at 1680 cm^{-1}) of its precursor was absent; ^{1}H-n.m.r. data ($CDCl_3$, 250 MHz): δ 3.86 (m, 2 H, H-6), 4.44 (m, 1 H, H-5), 5.0 (m, 1 H, H-4), 5.5 (d, 1 H, H-3), 2.86 (s. 2 H, 2 OH), 4.66 (s, 1 H, OH), and 7.0–7.5 (m, 5 H, phenyl). The configuration of C-3 was determined by the high value of the coupling constant for H-3 and H-4 ($J_{3,4}$ 7.5 Hz). The mass spectrum of **2** showed a small, molecular-ion peak at *m/z* 266, corresponding to a molecule resulting from the addition of a molecule of hydrogen to the C-3 carbonyl group.

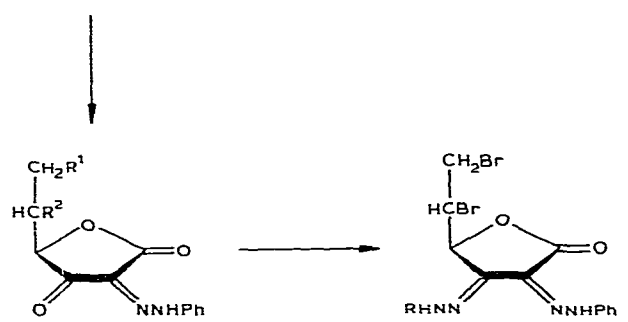
Acetylation of **2** with boiling acetic anhydride, or with acetic anhydride–pyridine, afforded a mono-*O*-acetyl derivative designated 5-*O*-acetyl-3,6-anhydro-L-*xylo*-2-hexulosono-1,4-lactone 2-phenylhydrazone (**3**); its elemental analysis agreed with the molecular formula $C_{14}H_{14}N_2O_5$, and its ^{1}H-n.m.r. spectrum showed only one *O*-acetyl group signal, at δ 2.08, in addition to those for the expected protons. Its mass spectrum showed a strong, molecular-ion peak at *m/z* 290.

†To whom inquiries should be addressed.
*On leave of absence from The Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt.

0008-6215/82/0000–0000/$02.75



1 2 3



4 R^1 = Br, R^2 = OH
5 R^1 = R^2 = Br

6 R = Ph
7 R = $C_6H_4NO_2$-*p*
8 R = $CONH_2$
9 R = $CSNH_2$

Treatment of compound **1** with hydrogen bromide in acetic acid did not give the monobromodeoxy derivative (**4**) expected, but a product having m.p. 155–156° was obtained, and identified as 5,6-dibromo-5,6-dideoxy-L-*threo*-2,3-hexodiulosono-1,4-lactone 2-phenylhydrazone (**5**) on the basis of elemental analysis, and i.r.-, n.m.r.-, and mass-spectral data. Compound **5** had no i.r. absorption for hydroxyl, and showed a carbonyl absorption at 1750 cm^{-1} (lactone) in addition to a carbonyl absorption at 1680 cm^{-1} (C-3); ^{1}H-n.m.r. data ($CDCl_3$, 250 MHz): δ 4.0 (m, 2 H, H-6), 4.80 (m, 1 H, H-5), 5.36 (d, 1 H, H-4), and 7.3–7.8 (m, 5 H, phenyl). The mass spectrum of **5** showed a molecular-ion peak at *m/z* 388, 392, appearing as two peaks having almost the same intensity due to the equal abundance of the two isotopes of bromine.

Treatment of **5** with phenyl- or (*p*-nitrophenyl)-hydrazine afforded the corresponding bis(hydrazones) **6** (m.p. 118–120°) and **7** (m.p. 198–200°), respectively. Similarly, treatment of **5** with semicarbazide or with thiosemicarbazide gave the 2-phenylhydrazone 3-semicarbazone **8** (m.p. 183–185°) and the 2-phenylhydrazone 3-(thiosemicarbazone) **9** (m.p. 150–151°), respectively.

REFERENCES

1 F. Micheel and K. Hesse, *Ber.*, 69 (1936) 879–881.
2 F. Micheel and R. Mittag, *Hoppe-Seyler's Z. Physiol. Chem.*, 247 (1937) 34.
3 M. A. El Sekily, S. Mancy, I. El Kholy, E. S. H. El Ashry, H. S. El Khadem, and D. L. Swartz, *Carbohydr. Res.*, 59 (1977) 141–149.
4 M. A. El Sekily, *Pharmazie*, 34 (1978) 531–534.
5 E. S. H. El Ashry, M. M. A. Abd El-Rahman, S. Mancy, and Z. M. El Shafei, *Acta Chim. Acad. Sci. Hung.*, 95 (1977) 409–415.
6 E. S. H. El Ashry, Y. El Kilany, and F. Singab, *Carbohydr. Res.*, 56 (1977) 93–104.