Journal of Labelled Compounds and Radiopharmaceuticals - Vol. XX, No. 4 523

PHOTOCHEMICAL ENRICHMENT OF DIACETYL [15-^{3}H] GIBBERELLIN-A_3-7-ALDEHYDES BY A TRITIUM ISOTOPE EFFECT[1]

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SUMMARY

During photocyclisation of 15α- and 15γ-tritiated diacetylgibberellin-A_3-7-aldehydes to the cyclobutanols we found an enrichment of the tritium labelled starting aldehydes by an isotope effect. The mechanism of the sterically controlled abstraction of the 15α-hydrogen/tritium-atom is discussed.

Keywords: Photochemical enrichment, tritium isotope effect, gibberellins

INTRODUCTION

Tritium-labelled gibberellin-A_3 (GA_3) has been obtained in very low yields by using either the WILZBACH method [2] or by heterogeneously catalyzed exchange reactions [3,4]. Recently, we reported chemical methods for the preparation of specifically labelled [6-^{3}H]GA_3 [5], [15α-^{3}H]GA_3, and [15γ-^{3}H]GA_3 [6]. The latter two were prepared by oxidation and deacetylation of the correspondingly labelled diacetyl-gibberellin-A_3-7-aldehydes <u>1b</u> or <u>1b</u> and <u>1c</u>. In this communication we wish to report a method for the photochemical enrichment of diacetyl [15-^{3}H]gibberellin-A_3-7-aldehydes.

0362-4803/83/040523-04$01.00
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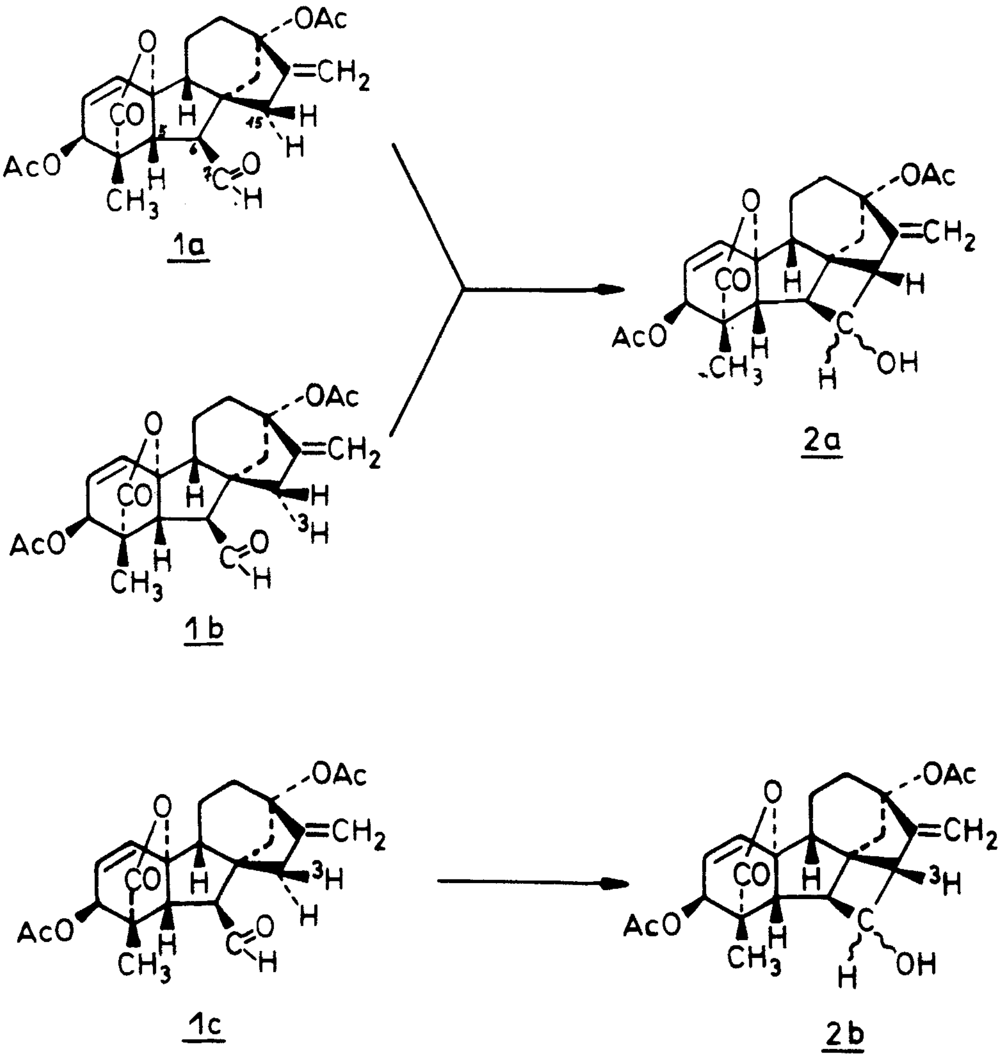
Received October 27, 1982



RESULTS AND DISCUSSION

The cyclization of diacetyl $[15\xi\text{-}^3H]GA_3$-7-aldehyde (mixture of 1a, 1b and 1c; specific activity 50 MBq/mmol) was induced by UV-irradiation in benzene. Chromatography of the reaction mixture afforded 68 % cyclobutanols 2a and 2b together with 20 % unreacted starting material. The 2a/2b mixture gave the specific activity of 26 MBq/mmol whereas that of the starting material during the reaction raised up to the unexpected higher value of 84 MBq/mmol. On the basis of mechanistic consideration one may assume the 15α-hydrogen to react with the $n \longrightarrow \pi^*$ excited state of the 6β-CHO function of diacetyl-GA_3-7-aldehyde. Obviously, the 15α-hydrogen in 1a and 1c reacts more rapidly than the more firmly bound 15α-tritium in 1b. As a result the labelled species 1b is enriched in the starting material.

This was established by UV-irradiation of the specifically labelled diacetyl[15α-^{3}H]GA_3-7-aldehyde (1a and 1b; specific activity 5.3 MBq/mmol). After chromatography 21 % of the starting aldehyde (1a and 1b) were recovered with a specific activity of 9.1 MBq/mmol while the epimeric cyclobutanols (2a; 60 % yield) showed only 43 kBq/mmol. This result indicates a relatively low isotope effect k_H/k_T of 1.53 and establishes a sterically controlled abstraction of the 15α-hydrogen/tritium-atom in the course of the cyclization.

EXPERIMENTAL

Diacetyl[15ξ-^{3}H]GA_3-7-aldehyde [6] (mixture of 1a, 1b, and 1c; 558 mg ≙ 1.35 mmol; 50 MBq/mmol) dissolved in dry benzene (50 ml) was irradiated with UV-light (mercury high pressure lamp; 25 h at 25-30 °C) in a quartz flask under an atmosphere of nitrogen. After addition of CH_3OH the labile tritium (8.2 MBq) was removed by repeated evaporations in vacuo. SiO_2 chromatography afforded diacetyl[15ξ-^{3}H]GA_3-7-aldehyde (112.1 mg; 84 MBq/mmol; elution with n-hexane/chloroform 4 : 6) and the cyclobutanols 2a and 2b (380 mg; mixture of 90 % 7α-OH and 10 % 7β-OH epimer [6,7]; 26 MBq/mmol; elution with n-hexane/chloroform 3 : 7).

According to the first preparation diacetyl[15α-^{3}H]GA_3-7-aldehyde [6] (1a and 1b; 41.6 mg ≙ 0.1 mmol; 5.3 MBq/mmol) in benzene (5 ml) was irradiated with UV-light (25 h at 25 - 30 °C). Analogous working up (282 kBq labile tritium) and chromatography gave diacetyl[15α-^{3}H]GA$_3$-7-aldehyde (8.7 mg; 9.1 MBq/mmol) and 2a (25 mg; 43 kBq/mmol).

REFERENCES

1. "Gibberellins" part 93, for part 92 see Lischewski, M. - Z. Chem. 22: 311 (1982); at the same time "Photochemical Reactions" part 38 (for part 37, see Lischewski, M. - Tetrahedron in preparation)
2. Baumgartner, W.E., Lazer, L., Dalzul, A.M., Cardinal, E.A., and Varner, E.L. - J. Agric. Food Chem. 7: 422 (1959)
3. Ayrey, G. and Chapman, J.M. - J. Lab. Comp. 16: 887 (1979)
4. Nadeau, R. and Rappaport, L. - Phytochemistry 13: 1537 (1974) and ibid. 11: 1611 (1972)
5. Lischewski, M., Adam, G., Liebisch, H.-W. and Pleiß, U. - J. Lab. Comp. 19: 725 (1982)
6. Lischewski, M. and Adam, G. - J. Lab. Comp. 19: 1231 (1982)
7. Lischewski, M. - Tetrahedron in preparation