

## Direct conversion of 2,4-dinitrophenylhydrazone of palmitaldehyde to its dimethyl acetal

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**SUMMARY** A simple procedure is described for the direct conversion of the 2,4-dinitrophenylhydrazone of palmitaldehyde to the corresponding dimethyl acetal, using  $\text{BF}_3$ -methanol reagent or 10% methanolic HCl in the presence of a keto compound.

**KEY WORDS** palmitaldehyde · dinitrophenylhydrazone · dimethyl acetal · conversion ·  $\text{BF}_3$ -methanol · methanolic HCl

THE SYNTHESIS OF UNSATURATED long-chain fatty aldehydes by oxidation of the corresponding fatty alcohol tosylates by dimethyl sulfoxide was recently reported from this laboratory (1). The aldehydes were isolated from the reaction mixture as 2,4-dinitrophenylhydrazones. Schogt, Begemann, and Recourt (2) liberated bound aldehydes of neutral milk fat in an acid medium and isolated the aldehydes as 2,4-dinitrophenylhydrazones. The free aldehydes were regenerated from the dinitrophenylhydrazones by refluxing with glacial acetic acid-levulinic acid-water mixtures at 120–130° for 45 min.

Aldehydes are frequently analyzed by gas-liquid chromatography (GLC) after being converted to dimethyl acetals (3, 4). Morrison and Smith (5) prepared the fatty acid methyl esters and dimethyl acetals from lipids with  $\text{BF}_3$ -methanol and analyzed the mixture by GLC. Farquhar (6), on the other hand, methanolized the lipids in 5% methanolic HCl and separated the dimethyl acetals from the methyl esters before subjecting each fraction to gas-liquid chromatographic analysis. Eng, Lee, Hayman, and Gerstl (7) achieved this separation by thin-layer chromatography.

The isolation of aldehydes from reaction mixtures during their syntheses or from natural sources as 2,4-dinitrophenylhydrazones possesses several advantages. Being crystalline derivatives, they can be easily separated and purified by recrystallization. Direct analysis by GLC of these derivatives has not been successful except in the case of short-chain aldehydes (8). Generally, the aldehydes are regenerated from their dinitrophenylhydrazones according to methods described by Keeney (9) and Schogt et al. (2) and the aldehydes are either converted to dimethyl acetals or oxidized to acids which are converted into methyl esters for analysis by GLC. The disadvantages of this method are that the aldehydes may be incompletely regenerated from their dinitrophenyl-

hydrazones; high temperatures and large amounts of reactants must be used; and many chemical manipulations are necessary.

This paper reports a convenient procedure for the direct conversion of the 2,4-dinitrophenylhydrazone of palmitaldehyde to its dimethyl acetal in high yield. Use of large volumes of solvents and high reaction temperatures are avoided, and the aldehyde need not be initially isolated. The method involves the removal of the 2,4-dinitrophenylhydrazone group by transfer to a keto compound in the presence of  $\text{BF}_3$ -methanol reagent or 10% methanolic HCl, so that the liberated aldehyde is immediately converted to the dimethyl acetal. This method is being applied to the identification and analysis of aldehydes bound in phospholipid plasmalogens and "neutral" plasmalogens from various sources.

### PROCEDURE AND RESULTS

Palmityl alcohol was converted to its tosylate, which was oxidized with dimethyl sulfoxide. The palmitaldehyde was isolated as its 2,4-dinitrophenylhydrazone as described by Mahadevan (1), and converted to the dimethyl acetal by one of the following methods:

*Procedure A: Using Levulinic Acid.* The dinitrophenylhydrazone, 50 mg, was mixed with 5 ml of  $\text{BF}_3$ -methanol reagent<sup>1</sup> (or 10% methanolic HCl) and 1 ml of levulinic acid in a 19/22 round-bottomed test tube and refluxed at 85° for 45 min. The resulting solution was cooled to 0°. After the addition of 5 ml of 5 N 90% methanolic NaOH, the solution was refluxed again for 20 min in order to saponify the methyl ester of levulinic acid, and cooled. The solution was twice extracted with 50 ml portions of petroleum ether (bp 30–60°). The combined extracts were washed once with distilled water. The slightly yellow solution was decolorized with charcoal, dried over a mixture of anhydrous  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$ , and filtered. The colorless solution was evaporated to dryness under high vacuum. The yield of palmitaldehyde dimethyl acetal was 28.8 mg (84%).

*Procedure B: Using Acetone.* In the above reaction the levulinic acid was replaced by 5 ml of acetone. After refluxing for 45 min the resulting solution was cooled to 0°, neutralized with 2 ml of 5 N 90% methanolic NaOH, and extracted with petroleum ether. The dimethyl acetal was recovered from the petroleum ether extract as described in Procedure A. Yield, 26.3 mg (77%).

Free palmitaldehyde was regenerated from its dinitrophenylhydrazone by the method described by Schogt et al. (2) and converted to dimethyl acetal by  $\text{BF}_3$ -methanol reagent as described by Morrison and Smith (5). The dimethyl acetals prepared thus and by

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the direct methods described above were subjected to thin-layer chromatographic and gas-liquid chromatographic analyses and were found to be identical.

The dimethyl acetal of oleyl aldehyde can also be prepared by the methods described, using an atmosphere of nitrogen. Details of the preparation and of the separation by GLC of the dimethyl acetals of other saturated and unsaturated fatty aldehydes will be described later.

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#### REFERENCES

1. Mahadevan, V. *J. Am. Oil Chemists' Soc.* **41**: 520, 1964.
2. Schogt, J. C. M., P. H. Begemann, and J. H. Recourt. *J. Lipid Res.* **2**: 142, 1961.
3. Gray, G. M. *Biochem. J.* **70**: 425, 1958.
4. Gray, G. M. *J. Chromatog.* **4**: 52, 1960.
5. Morrison, W. R., and L. M. Smith. *J. Lipid Res.* **5**: 600, 1964.
6. Farquhar, J. W. *J. Lipid Res.* **3**: 21, 1962.
7. Eng, L. F., Y. L. Lee, R. B. Hayman, and B. Gerstl. *J. Lipid Res.* **5**: 128, 1964.
8. Soukup, R. J., R. J. Scarpellino, and E. Danielczik. *Anal. Chem.* **36**: 2255, 1964.
9. Keeney, M. *Anal. Chem.* **29**: 1489, 1957.