

Reduction of Glyceride Oils to Fatty Alcohols with Sodium Borohydride-*t*-Butanol-Methanol

Y. Rajeswara Rao, A.J. Pantulu and G. Lakshminarayana*

Regional Research Laboratory, CSIR, Hyderabad 500007, India

Various glyceride oils were reduced to fatty alcohols by refluxing them with sodium borohydride in a mixture of *t*-butanol and methanol. Chemical characteristics and infrared spectral analyses showed the products to consist mainly of alcohols and the unreduced oils. Olefinic unsaturation was not affected. Castor, coconut and mustard oils yielded 89, 84 and 60% alcohols, respectively, and cottonseed, safflower, linseed, soybean and *Hydnocarpus wightiana* seed oils yielded 72–78% alcohols.

Glyceride oils and simple esters have been reduced to fatty alcohols with either sodium-alcohol (1), lithium aluminum hydride (2), or by catalytic hydrogenolysis. The simple esters were reported to be reduced to alcohols with sodium borohydride, a milder reagent, but only in the presence of a suitable solvent (diglyme, monoglyme, PEG-400, methanol, *t*-butanol) with or without addition of an activating agent (AlCl₃, LiBr, benzylphenylamine) (3–10). Among the methods reported, the addition of methanol to a mixture of sodium borohydride and fatty acid ester in refluxing *t*-butanol appears to be convenient (8). We have earlier reported that this method is useful in reduction of fatty acid methyl esters with various functional groups (11). This communication is an extension of the method to different glyceride oils.

EXPERIMENTAL

Sodium borohydride was purchased from Loba-Chemie Indoaustranal Co., Bombay. Methanol and *t*-butanol were laboratory reagent grade and redistilled. Oils were purchased and their characteristics are given in Table 1.

The method of reduction of oils to alcohols is basically the same as that of Soai et al. (8). To a mixture of oil

(1 milli saponification equivalent) and sodium borohydride (2.5 millimoles) in *t*-butanol (4.0 ml) under reflux, methanol (0.8 ml) was added over a period of one hr. For example, quantities of reagents taken for reduction of 6.0 g of castor oil were 1.85 g of sodium borohydride, 78.1 ml of *t*-butanol and 15.6 ml of methanol. After refluxing the mixture for an additional hour, it was cooled and water was added to quench the reaction. Methanol and *t*-butanol were removed under reduced pressure on a water bath. After cooling the aqueous solution, it was extracted with diethyl ether (3 × 25 ml). The combined extracts were dried over anhydrous sodium sulfate and the solvent was removed in a rotary evaporator. The product was analyzed for saponification, iodine and hydroxyl values according to AOCS methods (12) and by infrared spectroscopy (IR) as liquid film on a Perkin-Elmer Model 283. Mixed fatty alcohols were obtained from the products by saponification, followed by extraction with diethyl ether.

DISCUSSION

The IR spectra of the reduced products showed bands due to associated hydroxyls (3360 cm⁻¹) and did not show any band at 965 cm⁻¹ due to *trans* unsaturation. The IR spectrum of the product obtained by reduction of *H. wightiana* oil showed a band at 1610 cm⁻¹ due to skeletal vibrations of the cyclopentenyl ring.

The results of analyses of oils and their reduced products are given in Table 1. The extent of reduction of oils to alcohols was calculated on the basis of saponification values of oils and their reduced products. Coconut and castor oils yielded higher conversions (ca. 84.5% and 88.8%) than the other oils. However, increased carbon chain-length decreased the extent of reduction (e.g.,

TABLE 1

Reduction of Glyceride Oils with Sodium Borohydride-*t*-Butanol-Methanol to Fatty Alcohols

Oil reduced	Characteristics of oil and reduced product							% Reduction ^a
	Saponification value (SV)		Hydroxyl value		Iodine value			
	Oil	Reduced product	Oil	Reduced product	Oil	Reduced product		
Coconut	258.0	40.0	—	245.1	7.9	8.3	84.5	
Cottonseed	197.4	45.0	—	163.7	112.9	117.2	77.2	
Safflower	194.7	46.9	—	160.5	146.4	146.1	75.4	
Mustard	178.3	71.7	—	115.4	121.0	125.2	59.8	
Linseed	193.6	49.2	—	158.2	171.5	179.6	74.6	
Soybean	190.0	53.0	—	153.4	124.6	131.4	72.1	
Castor	182.6	20.5	162.1	329.1	85.6	88.4	88.8	
<i>Hydnocarpus wightiana</i>	198.8	44.1	—	170.8	103.4	106.3	77.8	

^a(SV of oil - SV of reduced product) × 100/SV of oil.

*To whom correspondence should be addressed.

mustard vs other oils). Solubility of oil thus seems to play a role in the yield of alcohols.

The sodium-alcohol method is laborious, the lithium aluminum hydride method is hazardous and high pressure catalytic hydrogenolysis leads to saturation and isomerization of double bonds, and dehydroxylation. The sodium borohydride-*t*-butanol-methanol method seems to be advantageous for the reduction of glyceride oils over these other methods. The method is simple, convenient and suitable for reduction of glyceride oils having different functional groups in their fatty acid moieties.

ACKNOWLEDGMENT

The Council of Scientific and Industrial Research, New Delhi, awarded a Research Fellowship to YRR.

REFERENCES

1. Hansley, V.L., *Ind. Eng. Chemistry* 39:55 (1947).
2. Micovic, V.M., and M.Lj. Mihailovic, *Lithium Aluminium Hydride in Organic Chemistry*, Monograph series, Vol. 237, edited by K.V. Petkovic, Serbian Academy of Sciences, 1955, pp. 34-44.
3. Brown, H.C., and S.K. Murthy, *Tetrahedron* 34:567 (1969).
4. Wigfield, D.C., S. Feiner and F.W. Gowland, *Tetrahedron Lett.* 3377 (1976).
5. Sell, C.S., *Aust. J. Chem.* 28:1383 (1975).
6. Santaniello, E., P. Ferraboschi and P. Sozzani, *J. Org. Chem.* 46:4584 (1981).
7. Kollonitsch, J., O. Fuchs and V. Gabor, *Nature* 175:346 (1955).
8. Soai, K., H. Oyamada and A. Ookawa, *Synth. Commun.* 12:463 (1982).
9. Brown, M.S., and H. Rapoport, *J. Org. Chem.* 28:3261 (1963).
10. Kikukawa, Y., *Japan Kokai* 76:115, 401 (1976); *Chem. Abstr.* 86:72240 (1977).
11. Rao, Y.R., A.J. Pantulu and G. Lakshminarayana, *Fat Sci. Technol.* 89:398 (1987).
12. Official and Tentative Methods of the American Oil Chemists' Society, 3rd edn., edited by W.E. Link, AOCS, Champaign, IL, 1973.

[Received November 15, 1988; accepted January 11, 1989]
[J5600]