

corresponding symmetrical diglycerides and crystallisation from light petroleum (6). Pure tripalmitin, mp 66.0, was used for comparison. The non-aqueous media employed were refined soybean oil, benzene, kerosene, heptane (bp 99–100) and white paraffin oil (33.5 centistokes at 21°C). All measurements were carried out at 50°C with 0.5% solutions of the various glycerides mentioned following the method D971-50 of the ASTM (1952) and applying the correction factors specified therein. Results are listed in Table I.

Conclusion

It appears that 2-monoglycerides are slightly more effective in reducing the interfacial tension of oil-water systems than 1-monoglycerides. There was no appreciable difference between the surface activity of 1,2- and 1,3-diglycerides in the case of soybean oil and benzene but the difference was quite pronounced in aliphatic hydrocarbons. Tripalmitin, as could be expected, had but little effect. These results indicate that free primary hydroxyl groups of glycerol reduce interfacial tension more than the secondary hydroxyl group.

Viewed from the practical angle, the presence of

2-monoglycerides in commercial monoglycerides enhances the surface activity of these products which adds support to the postulate (10) that their contents should not be disregarded. On the other hand the significance of 1,2-diglycerides is not pronounced and is further limited by the fact, that as shown by Feuge (11) the surface activity of diglycerides in the presence of monoglycerides is very small.

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Conversion of Oleyl and Elaidyl Tosylates to Aldehydes

THE SYNTHESIS of unsaturated aliphatic aldehydes by oxidation of the corresponding alcohols is seldom employed because conventional oxidizing agents not only oxidize the aldehyde to acid, but also attack the carbon-carbon double bond. Such aldehydes are usually prepared from the corresponding carboxylic acids either by Grundmann's synthesis (1) or via the acyloin condensation (2), both involving a number of steps.

Kornblum et al. (3) reported a simple procedure for the selective oxidation of benzylic tosylates and a saturated short-chain alkyl tosylate to aldehydes in yields of 75% by dimethyl sulfoxide. Whether this method is applicable for the synthesis of unsaturated aliphatic aldehydes has not been tested. The oxidation by dimethyl sulfoxide of the tosylates of oleyl alcohol and elaidyl alcohol to aldehydes is described here.

The oxidation of the tosylates is accomplished by heating them with a mixture of sodium bicarbonate and dimethyl sulfoxide at 160°C for five min. Heating the mixture at 135°C for 15 min resulted in lower yields. The products were isolated as the 2,4-dinitrophenyl hydrazones. Examination of the IR spectra of the 2,4-dinitrophenyl hydrazones of oleyl aldehyde and elaidyl aldehyde showed negligible *trans* absorption in the former and a pronounced band in the latter at 965 cm^{-1} , showing that under the experimental conditions no *cis-trans* isomerization occurred. However, preliminary experiments have shown that such changes occur at other reaction conditions. These results as well as the oxidation of polyunsaturated aliphatic alcohols to aldehydes will be reported later.

Experimental

Dimethyl sulfoxide was obtained from Matheson, Coleman and Bell and used without purification. Oleyl alcohol was obtained from The Hormel Institute. Elaidyl alcohol was prepared by reduction of methyl elaidate (The Hormel Institute) with LiAlH_4 .

The alcohols were converted to the tosylates with *p*-toluenesulfonyl chloride in pyridine as described by Baer et al. (4).

Oxidation of oleyl tosylate by dimethyl sulfoxide. A suspension of 1.1 g oleyl tosylate, 0.5 g sodium bicarbonate and 5 ml dimethyl sulfoxide was placed in a 100-ml round bottom flask fitted with a condenser and through which nitrogen was bubbling. The flask was immersed in a bath preheated at 160–5°C. After five min the reaction mixture was cooled rapidly to room temp and poured onto ice water. The precipitated material was extracted with ether, the ether extract washed once with water, dried over anhydrous sodium sulfate and filtered. The product after evaporation of ether was converted to the 2,4-dinitrophenyl hydrazone and crystallized from 95% ethanol. Yield 0.78 g (64%), mp 66–67°C [reported 65.5–66.5°C (1)].
Analysis calculated for $\text{C}_{24}\text{H}_{38}\text{N}_4\text{O}_4$: N, 12.54. Found: N, 12.52.

Oxidation of elaidyl tosylate was carried out exactly as described above. The 2,4-dinitrophenyl hydrazone of elaidyl aldehyde was obtained in 72% yield, mp 92.5–93.5°C [reported 90°C (5)].

Analysis calculated for $\text{C}_{24}\text{H}_{38}\text{N}_4\text{O}_4$: N, 12.54. Found: N, 12.56.

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