with dry ice-acetone. Sodium soaps of glutaric and adipic acids, and barium soaps of the other acids were prepared for infrared spectroscopy (22). Ethanol solutions of the free acids were titrated with 1 *N* sodium hydroxide to a phenolphthalein end point. The solutions were evaporated until thick slurries of salt remained. Acetone was added to the slurries and the insoluble material was filtered off. The soaps were washed twice by acetone and dried at 110C. To prepare the barium soaps, several mg of the free acids were dissolved in about 3 ml methanol and 1 ml 1% barium chloride dihydrate methanol solution was added. Concd aqueous ammonia (28%) was added dropwise to the hot methanol solutions until no additional precipitate was formed. The precipitate was centrifuged, washed twice with 3 ml portions hot methanol and dried at 110C. The soaps were used to make potassium bromide pellets and the IR spectra were identical with those of the pure specimens.

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• *Letters to the Editor*

Surface Activity of Symmetrical and Unsymmetrical Mono- and Di-glycerides

MIXTURES of mono-, di- and triglycerides prepared by glycerolysis of fats find application in producing oil in water emulsions for various purposes (edible, pharmaceutical, cosmetic, etc.). In the past 1-monoglycerides were considered the only active ingredients in such preparations, the presence of 2-monoglycerides being as a rule disregarded. However, it seems that commercially produced partial glycerides contain appreciable amounts of 2-monoglycerides (1,2,3). It appears also that diglycerides invariably present in commercial products comprise both 1,2- and 1,3-isomers (4,5). This could be expected since Crossley et al. (6) have shown that 1,2-diglycerides are by no means as unstable as was hitherto assumed and that the heating of symmetrical diglycerides leads to an appreciable formation of 1,2-isomers. The purpose of the present work was to compare the effects of symmetrical and unsymmetrical mono- and diglycerides on the interfacial tension of fat and hydrocarbon-water systems which could assist in the evaluation of the emulsifying properties of commercial monoglyceride preparations. At the same time this would be tantamount to a comparison between the effects of free primary and secondary hydroxyl groups of glycerol on the surface activity of partial glycerides.

Experimental

The measurements of the interfacial tension were carried out with a du Noüy tensiometer using a platinum ring 3.96 cm in circumference. The ratio of the diam of the ring to that of the wire was 41.0. The following partial glycerides were investigated: pure 1-monostearin, mp 81.5C prepared by a modified isopropylidene-glycerol method (7); 2-mono-stearin, mp 74.3C prepared essentially by Martin's method (8) and containing approx 3% of the 1-monoester; 1,3-dipalmitin mp 74.0, and 1,3-distearin, mp 79.5, prepared by direct esterification of glycerol with fatty acid chlorides in N,N dimethyl formamide-chloroform solution (9), 1,2-dipalmitin, mp 62.5 and 1,2-distearin, mp 68.0, prepared by heat isomerisation of

TABLE I

Interfacial Tension in dynes/cm at 50C of oil (hydrocarbon)-water systems with added glycerides (0.5% glyceride solution in non-aqueous medium)

Non-equeous medium	Control	Type of glyceride added						
		1-mono-stearin	2-mono-stearin	1,3-Di-stearin	1,2-Di-stearin	1,3-Di-palmitin	1,2-Di-palmitin	Tri-palmitin
Soybean oil	29.6	22.4	21.4	29.0	28.6	29.0	28.4	29.5
Benzene	35.6	22.1	20.4	34.1	32.8	33.8	33.3	35.2
Kerosene	50.0	5.1	2.9	39.7	27.3	38.1	24.9	46.4
n-Heptane	45.8	6.9	5.3	37.8	24.3	36.5	22.4	43.8
Paraffin oil	48.0	2.6	2.2	39.2	25.6	38.7	24.6	46.3

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 21C). All measurements were carried out at 50C 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 160C for five min. Heating the mixture at 135C 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 160–5C. 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 66–67C [reported 65.5–66.5C (1)].

Analysis calculated for $C_{24}H_{38}N_4O_4$: 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 92.5–93.5C [reported 90C (5)].

Analysis calculated for $C_{24}H_{38}N_4O_4$: N, 12.54. Found: N. 12.56.

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