TABLE I

Reaction of Methyl Oleate With Ammonia

Expt. No.	Temp., °C.	Time, Hours	Quantity of NH_3	Yield of Oleamide Isolated %	Special Conditions and Remarks
28% Aqueous Ammonia					
1	25	25	.....[a]	0	Oleic acid added in an amount equal to 2% by weight of methyl oleate.
2	25	25	.....[a]	0	Methanol present in an amount equal to that of methyl oleate.
3	100	6	.....[a]	0.7-2.5	Conducted both in absence and presence of 2% of oleic acid.
4	150	1	.....[a]	1	
5	150	3	.....[a]	25	
6	150	6	.....[a]	45	
7	150	6	.....[a]	50	2% of oleic acid present.
8	150	6	.....[a]	32	135 g. of ammonium chloride present per 100 g. of methyl oleate. Reaction product darkly colored.
9	175	6	.....[a]	50	Conducted both in absence and presence of 2% of oleic acid.
Anhydrous Liquid Ammonia					
10	25	6	.....[b]	Trace	
11	100	7	.....[c]	7.8-9.2	
12	135	6	.....[c]	40	
13	135	12	.....[c]	62	
14	165	6-12	.....[c]	86-90	The shorter time gave the slightly lower yield.
15	175	3	.....[c]	78	
16	175	6-12	.....[c]	85-89	
17	175	6	.....[d]	86	
18	200	6-12	.....[c]	79-83	Reaction product darkly colored.
19	200	12	.....[d]	75	Reaction product darkly colored.

[a] 900% excess.
[b] 3 ml. NH_3 : 2 ml. methyl oleate (approx. 22 moles NH_3 per mole methyl oleate)
[c] 1 ml. NH_3 : 1 ml. methyl oleate (approx. 15 moles NH_3 per mole methyl oleate)
[d] 1 ml. NH_3 : 2 ml. methyl oleate (approx. 7.5 moles NH_3 per mole methyl oleate)

Starting Materials. Beef fat (edible "oleo oil"): acid number, 0.8; saponification number, 195; iodine number, 43.7-39.7 (changed during storage and handling; polyunsaturated acids, 3.3% (2).

Olive oil (edible grade): acid number, 1.5; saponification number, 193; iodine number, 80.9.

Castor oil (U.S.P. grade): acid number, 2.1; saponification number, 183; iodine number, 86.1; hydroxyl, 4.79%.

Tobacco seed oil was prepared by extracting the ground tobacco seed with petroleum naphtha (hexane fraction) in a Soxhlet extractor. The solvent-free oil had the following characteristics: saponification number, 195; iodine number, 132.0.

Methyl oleate, iodine number, 83.5, methyl oleate content, 97.5%, was prepared by the esterification of purified oleic acid obtained from olive oil by multiple low-temperature fractional crystallization and distillation (3, 16).

n-Dodecylamine and monoethanolamine were obtained by fractional distillation of the purest commercial grades through efficient columns. They had the correct physical and chemical characteristics. Anhydrous liquid ammonia was the purest commercial grade. It was purchased in cylinders and was used without further purification. The 28% aqueous ammonia was the A.C.S. grade.

Preparation of Amides. Before investigating the reaction of fats with ammonia, a systematic study was conducted on the ammonolysis of methyl oleate. This compound was selected because the determination of yield is simpler when a single amide is produced and the reaction conditions can be translated directly to the ammonolysis of triglycerides.

Reaction of Methyl Oleate With 28% Aqueous Ammonia. Fifty-nine grams (0.2 mole) of methyl oleate and 123 g. of 28% aqueous ammonia (2.0 moles of NH_3) were placed in a specially constructed stainless steel bomb (400 ml. capacity), which was then rotated end over end in a thermostatically controlled oil bath (9). Experiments were conducted from 25° to 175°C. for various reaction times (Table I). After the bomb had cooled, the contents were transferred to a beaker and agitated while being warmed on the steam bath to expel excess ammonia. The mixture was then made slightly acid by the addition of 6N hydrochloric acid, and the melted layer of fatty material was washed with warm water until free of acid. It was then dissolved in petroleum naphtha (hexane fraction) (3 ml./g.), treated with activated carbon, and filtered. The filtrate was adjusted to 5 ml. of solvent per gram of solute and cooled to 0°C. to precipitate oleamide. Table I shows the results of these experiments. The yield of oleamide given is that isolated as precipitate from petroleum naphtha at 0°C. Based upon recrystallization experiments with crude and pure samples of oleamide, it is estimated that approximately 85 to 90% of the oleamide present was isolated.

Evaporation of the filtrate after separation of oleamide yielded a liquid product consisting almost entirely of free acids.

Reaction of Methyl Oleate With Liquid Ammonia. Thirty grams of methyl oleate (0.1 mole) were placed in a stainless steel bomb (400-ml. capacity) and cooled