conclusive. Further experiments are being carried out to test this possibility further.

CONCLUSIONS.

Using sleeping time as the criterion, acquired tolerance to amytal, pentobarbital, ortal, pernoston and evipal was investigated in rabbits. It was found that upon daily administration of ortal and evipal there was no significant change in the sleeping time. Tolerance to a certain degree was developed for pentobarbital, pernoston and amytal as evidenced by a significant decrease in sleep. The tolerance developed almost immediately following the first injection, and reached its limits in four to seven days.

It was found that the acquired tolerance disappeared rapidly after the ending of the daily injections and within 3 or 4 days the animal responded to the barbiturate in practically the same way as it had done to the first dose.

The destruction of amytal as determined by its rate of disappearance from the blood, liver and muscle appears to take place somewhat more rapidly in tolerant than in non-tolerant rabbits.

BIBLIOGRAPHY.

(1) Fitch, R. H., *J. Pharmacol.*, 39, 266 (1930).
(2) Ravdin, I. S., Drabkin, D. L., and Bothe, A. E., *J. Lab. Clin. Med.*, 16, 561 (1930).
(3) Deuel, H. V., Chambers, W. H., and Milhorat, A. T., *J. Biol. Chem.*, 69, 249 (1926).
(4) Nicholas, J. S., and Barron, D. H., *J. Pharmacol.*, 46, 125 (1932).
(5) Swanson, E. E., Weaver, M. M., and Chen, K. K., *Am. J. Med. Sci.*, 193, 246 (1937).
(6) Swanson, E. E., and Shonle, H. A., *J. Lab. Clin. Med.*, 16, 1056 (1931).
(7) Stanton, E. J., *J. Pharmacol.*, 57, 245 (1931).
(8) Moir, W. M., *Ibid.*, 59, 68 (1937).
(9) Carmichael, E. B., and Posey, L. C., *Proc. Soc. Exptl. Biol. Med.*, 30, 1329 (1933).
(10) Kennedy, W. P., *J. Pharmacol.*, 50, 347 (1934).
(11) Wagner, C. P., *J. Am. Med. Assoc.*, 101, 1787 (1933).
(12) Hoge, S. F., *Am. Med.*, 40, 235 (1934).
(13) *J. Am. Med. Assoc.*, 105, 1374 (1935).
(14) Schmitz, H. E., *Am. J. Obst. Gynecol.*, 33, 103 (1937).
(15) Koppanyi, T., Murphy, W. S., and Krop, S., *Arch. intern. pharmacodynamie*, 46, 76 (1933).
(16) Koppanyi, T., Dille, J. M., Murphy, W. S., and Krop, S., Jour. A. Ph. A., 23, 1074 (1934).

THE DETERGENT QUALITIES OF SOFT SOAPS.*

BY EDWIN J. RATHBUN AND EDWARD D. DAVY.[1]

This work was undertaken to determine the relative efficiency of soaps made from the common fixed oils and Oleic Acid which were thought best suited for a soft soap. The soft soap of the Pharmacopœia is very effective but somewhat objectionable because of its odor and color and is not generally used. Soaps made with Sodium and Potassium Hydroxides in the ratio indicated in the U. S. P. XI

* Presented before the Scientific Section, A. Ph. A., Minneapolis meeting, 1938.

[1] From the Department of Pharmaceutical Chemistry, School of Pharmacy, Western Reserve University.

for Sapo Mollis were prepared and the alkalinity adjusted to approximately 0.1%. Cottonseed oil soap was omitted as it tends to form a heavy precipitate with Sodium Hydroxide.

The various references cited show that detergency is dependent upon a number of factors, chief of which are:

1. Wetting ability.
2. Emulsifying power.
3. Deflocculating ability.
4. Attraction of detergent solution and the oil (dirt) for the surface of fiber or solid to be cleaned.
5. Kind of material or surface to be cleaned.
6. Types of dirt (grease and solids mixed).
7. Temperature of the water.
8. Characteristics of detergent molecules.
9. Agitation.

Foster Dee Snell (1) states that a detergent which has wetting power but lacks deflocculating and emulsifying power will merely cause dirt to spread over a surface more evenly rather than cause it to be removed permanently.

Rhodes and Wynn (2) show by washing tests using a 0.25% soap solution in a special machine designed for the purpose, using cotton cloth soiled with carbon black in Crisco and lubricating oil, that the addition of 0.25% sodium hydroxide at first increases and then decreases the detergent effect. Their results indicate that at p_H 9.66 and 60° C. the maximum washing effect is obtained. Rhodes and Bascom (3) found that a solution of p_H 10.7 at room temperature showed the greatest efficiency.

It is very difficult to set any fixed standard for determining detergency because so many factors are involved, but particularly the variations in the kinds of grease and dirt to be removed. Robinson (4) states that detergent action will be looked upon as the removal of oil or grease from a fiber (or other solid material). An emulsion of the oil is therefore necessary, since if the oil films were merely displaced and floated on the surface of the water, then upon removal of the cloth or other object it would again become covered with oil film.

It is very apparent from the practical application that wetting ability and emulsifying power are the chief factors affecting detergency. The following oils made into soft soaps with sodium and potassium hydroxides were compared: Corn, soya bean, cocoanut, linseed and brands of commercial oleic acid which will be designated "a," "b" and "c." The oleic acids contained a considerable proportion of non-saponifiable matter and they produced distinctly colored soaps. Surface tension measurements were taken with a Du Nuoy Tensiometer starting with a liquid soap representing 16.8% anhydrous soap which is about the maximum that can be put into solution and maintain proper fluidity. Cocoanut oil soap may be in somewhat higher concentration.

The percentage of the original soap solution 16.8% excludes the glycerin formed from the oils. This was calculated using a definite weight of oil and basing the calculation on triolein. Because of the lower molecular weight fatty acids in cocoanut oil, it requires more alkali for saponification. This gives cocoanut oil a distinct advantage over the other oils since the same weight of oil was used to produce a given weight of soap in each case.

Saponification No. Cocoanut Oil 258.

Saponification No. Cottonseed Oil average 194, which approximates that of most fixed oils.

It will be noted that the S. T. reached the lowest point at a dilution of 0.2% anhydrous soap. The alkalinity cannot be said to influence it since at this dilution the solutions are approximately at p_H 10.

TABLE I.

% Anhydrous Soap.	16.8.	4.2.	1.05.	0.21.	0.0105.	0.0052.	0.0021.	0.00105.
	Surface Tensions, Dynes per Cm. Temperature, 22° C.							
Corn	35.8	34.4	29.7	28.4	34.6	38.0	40.6	44.6
Soya bean	38.4	33.5	32.0	27.8	33.0	37.2	40.8	43.2
Cocoanut	36.0	34.5	30.0	25.9	32.8	35.8	41.8	54.1
Linseed	33.7	34.7	33.5	28.8	37.3	41.5	42.7	44.0
Oleic acid a	33.3	32.2	30.0	27.5	30.8	38.4	40.6	52.4
Oleic acid b	31.9	33.1	30.6	27.9	33.3	37.6	42.3	50.3
Oleic acid c	32.0	33.1	30.7	28.1	34.4	38.4	42.3	48.7
					p_H.			
Corn	11.2	10.9	10.7	9.3	8.1	7.5	6.3	6.4
Soya bean	11.3	10.9	10.8	9.8	8.6	7.95	6.9	7.0
Cocoanut	10.6	10.5	10.3	10.2	7.6	7.2	6.9	6.5
Linseed	10.1	10.3	9.8	9.3	8.1	7.37	6.8	6.4
Oleic acid a	10.8	10.2	9.7	9.9	8.6	8.0	7.1	7.1
Oleic acid b	10.8	10.7	10.6	10.4	8.5	7.5	6.8	6.5
Oleic acid c	11.1	10.2	9.8	9.4	8.4	7.7	6.7	6.4

The ability of these soaps to emulsify mineral oil was judged by the aqueous liquid which separated from the emulsion, using various dilutions of soap. The oleic acid soaps were excluded. The separation of aqueous liquid was recorded at intervals of 45 minutes and 90 minutes with the exception of the 12% soap solution which separated more slowly and was read at intervals of 45 minutes and 2 hours. Soaps made from a mixture of cocoanut oil 20% with soya bean and cottonseed each 80% were also included for their emulsion values. The tables also include soaps made with potassium hydroxide only, which admits the use of cottonseed oil. The potash soaps may be made of proper fluidity to contain 24% anhydrous soap.

The emulsions were made by adding all the oil at once and the mixing kept constant at 1.5 minutes. The emulsifier was provided with a close-fitting top which supported the motor and shaft and had an opening only for introducing the oil. This confined the emulsion swell to the limits of the container since no more air was admitted, the capacity of the mixing bowl being one pint. The emulsion was poured several times from one container to another in order to insure uniform sampling, after which 100 cc. was poured into a graduated cylinder and the separated liquid noted. Time of mixing affects the separation so that one must adhere to a constant time factor.

It will be noted in Table II that a high percentage of soap, 12% shows less separation, but emulsification appears no more complete than that from 1.6% and 0.2% soap. The series at 0.2% concentration was made since at this point surface tension is lowest. The more permanent emulsion, however, results from a 12% soap, probably as a result of increased viscosity.

It should also be noted that cocoanut oil soap produces in practically every instance an emulsion which breaks a little more rapidly than those made from the other fixed oils. The opposite conception I believe is normally held because of the increased amount of lather produced by cocoanut oil soaps over that of others. It is undoubtedly true that if a hard water were used cocoanut oil soaps would show a distinct advantage. Among the other oils there is no perceptible advantage of one over the other.

TABLE II.

Sodium-Potassium Soaps. 100-Cc. Soap Solution. 50-Cc. Oil.

Mixing Time, 3 Minutes.	% Anhydrous Soap.	45-Min. Interval.	90-Min. Interval.
Cocoanut	1.6	13.0 cc.	14.0 cc.
Soya bean	1.6	13.5 cc.	15.0 cc.
Corn	1.6	14.0 cc.	15.0 cc.
Linseed	1.6	14.0 cc.	14.5 cc.

Potassium Soaps. 100-Cc. Soap Solution. 50-Cc. Oil.

Mixing Time 1.5 Minutes.	% Anhydrous Soap.	45-Min. Interval.	90-Min. Interval.
Cocoanut	1.6	15.0 cc.	15.5 cc.
Soya bean	1.6	13.5 cc.	14.5 cc.
Cottonseed	1.6	14.0 cc.	15.0 cc.
Cocoanut 20 Soya bean 80	1.6	14.0 cc.	15.0 cc.
Cocoanut 20 Cottonseed 80	1.6	14.0 cc.	15.0 cc.

Potassium Soaps. 50-Cc. Soap Solution. 50-Cc. Oil.

Mixing Time, 1.5 Minutes.	% Anhydrous Soap.	45-Min. Interval.	2-Hour Interval.
Cocoanut	12	2 cc.	4 cc.
Soya bean	12	1 cc.	3 cc.
Cottonseed	12	1 cc.	3 cc.

100-Cc. Soap Solution. 50-Cc. Oil.

Mixing Time 1.5 Minutes.	% Anhydrous Soap.	45-Min. Interval.	90-Min. Interval.
Cocoanut	0.2	16.5 cc.	17.0 cc.
Soya bean	0.2	14.0 cc.	14.5 cc.
Cottonseed	0.2	14.5 cc.	15.0 cc.

The requisites of a soft soap base should include general availability of the oil within a reasonable price range, freedom from objectionable odor and color, and should represent a single oil. A single oil is desirable because chemical and physical constants which might be set up for a mixture of oils, permit mixtures to be made meeting these requirements yet not representing the particular formula indicated. Iodine and acid values can be calculated so that when mixed will produce any desired values. Solidifying points do not follow any particular pattern when one lower is mixed with one higher but by careful manipulation mixtures may be made meeting the three values commonly set up as standards.

A single oil moderately priced for the preparation of a soft soap will, without doubt, be welcomed by the manufacturers of soap. Advantages of one fixed oil over another or of a mixture of oils for detergency is questionable as no one has as yet devised a means for properly evaluating them. Cocoanut oil soap, by the emulsion test, is definitely over-rated.

Soya bean soap (5) compares favorably with linseed oil in emulsifying ability but has somewhat the same objection as has been raised to linseed oil soaps. Soya bean soaps from refined oil develop a distinctive odor and darken considerably with age.

Cocoanut oil soaps have been credited with producing skin irritations when used by some persons while others show no reaction to it. It is significant, however, that upon inquiry in some hospitals where they purchase soap containing a high percentage of cocoanut oil that they also purchase another without cocoanut oil for the more special uses, such as in the surgery and for maternity hospital use.

We have set up standards for the University Hospitals' liquid soap, used for the past fifteen years without any complaints. Soap used as a lubricant is sterilized before use. This soap has been made of cottonseed oil and potassium hydroxide and the alkalinity when reduced to terms of soft soap shall not exceed 0.03%. Very often the soap has an acid reaction when a portion of the water is evaporated and the residue dissolved in alcohol, phenolphthalein indicator. Free fatty acids or oil are objectionable because of the tendency to rancidity.

For the reasons enumerated we would recommend that soft soap be made from cottonseed oil as follows:

SAPO MOLLIS.

Cottonseed oil	510 Gm.
Potassium hydroxide	103 Gm.
Distilled water	120 cc.

Dissolve the potassium hydroxide in the water and add it to the oil. Mix and allow to stand with occasional mixing until a small portion of the soap, when dissolved in distilled water, makes a clear solution. Adjust the alkalinity so that it shall not exceed 0.04%. Add water to 1000 Gm. This approximates a 60% soap.

A demand exists for a soap containing some cocoanut oil because of its added lathering qualities, and we would recommend a second soap preferably to consist of 20% cocoanut oil in 80% cottonseed oil for general use in soap service.

SAPO MOLLIS POPULARIS.

Cottonseed oil	408 Gm.
Cocoanut oil	102 Gm.
Potassium hydroxide	109 Gm.
Distilled water	120 cc.

Directions as for Sapo Mollis.

LIQUOR CRESOLIS SAPONATUS.

Cottonseed oil	350 Gm.
Potassium hydroxide	71 Gm.
Distilled water	90 cc.

Saponify as directed for Sapo Mollis.

Add cresol	500 cc.
Distilled water to	1000 cc.

Saponification of the oil is incomplete in the presence of cresol. Addition of the cresol to the neutral soap makes a product brilliantly clear, and may be diluted as desired without clouding the solution.

REFERENCES.

(1) *Ind. Eng. Chem.*, 25, 162 (1933).
(2) *Ibid.*, 29, 55 (1937).
(3) *Ibid.*, 23, 778 (1931).
(4) "Wetting and Detergency," Chem. Pub. Co., 137 (1937).
(5) *Chem. and Ind.*, 691–693 (1936), through *Chem. Abs.*, 30, 7374 (1936).