Determination of Acetyl Values

Sir:

The determination of acetyl values of acetylated fatty acids as described in the "National Formulary," 12th ed. (1), was adapted from the derivation by Cook (2). This procedure is also very useful where hydroxyl groups exist together with esters. Cook's derivation provides a mathematical correction for the molecular weight difference between an original fatty material and the acetylated product and requires the determination of the saponification values of both materials.

The equation employed by the N.F. substitutes the acid value of the unacetylated free fatty acid for the saponification value of the original fatty substance in the Cook formula. The acid value of a free fatty acid is equivalent to its saponification value since there are no esters present. The N.F. equation, however, is incorrect in the denominator term. Since the correct denominator is a function of the saponification value *of the original fatty substance* (not the acetylated product), the proper denominator should be based on the acid value of the free fatty acids. The correct equation is

$$A = S - F/1 - 0.00075\ F$$

where A is the acetyl value of the acetylated fatty acids, S is the saponification value of the acetylated fatty acids, and F is the acid value of the original fatty acids. The existing official formula gives values which are 10 to 15% high for usual monohydroxylated fatty acids. Di- and trihydroxylated fatty acids show progressively higher deviations. The corrected formula above is in exact agreement with theoretical values in all cases. The term "A" is incorrectly defined in the monograph as the acetyl value of the *free* acid. This term must be the acetyl value of the *acetylated* fatty acid which would be in agreement with the N.F. definition of acetyl value and with the Cook formula derivation.

In the specific case of fatty acids, it is also possible to further simplify the calculations and the analytical procedure since all saponifiable groups are hydrolyzed prior to acetylation. The absence of interfering mixed anhydrides referred to by Warth (3) is assured since the acetylated product is purified by twice boiling in water. After saponification of the fatty material and acetylation of the fatty acids, it is only necessary to determine the ester value of the acetylated product as described in the N.F. In this case, ester value and acetyl value are identical. If acetylated fats, oils, waxes, or similar substances containing ester groups other than acetyl are used, the official methodology must be employed.

Results obtained using the official procedure and ester value determinations are compared to theoretical acetyl values in Table I for acetylricinoleic acid and cholesterol acetate.

Table I.—Acetyl Values

Compd.	Theoretical	Official Method[a]	As Ester Value
Acetylricinoleic acid	164.76	163.13	162.41
Cholesterol acetate	130.86	136.26	123.65

[a] Corrected formula.

Since the procedure described in the N.F. is very reliable and applicable to a wide variety of fatty materials, the scope of the monograph could be expanded to include these substances. The formula for calculation of results and the definition of the term "A" should be corrected as indicated.

(1) "National Formulary," 12th ed., Mack Publishing Co., Easton, Pa., 1965, p. 451.
(2) Cook, L. W., *J. Am. Chem. Soc.*, 44, 392(1922).
(3) Warth, A. H., "The Chemistry and Technology of Waxes", 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1956, p. 593.

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