moiety of tung oil by means of the Diels-Alder reaction. Moderate quantities of methyl vinyl ketone-methyl *alpha-* and methyl *beta*-eleostearate adducts have been prepared in good yields. A portion of the former material has been subjected to aromatization and selective oxidation in establishing a proof that the reaction proceeds by the Diels-Alder addition. A sample of the methyl vinyl ketone-methyl *alpha*-eleostearate adduct has been fractionally crystallized and one of its two positional isomers isolated in pure form. A semicarbazone derivative of this isomer has also been prepared.

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An Extrapolation Procedure for Determining Solubilities of Mixtures

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DIFFERENCES in solubility form the basis for the resolution of many complex mixtures of chemical compounds into simpler ones. In some cases the solubility characteristics of the substances present are so different that the desired separation can be achieved by exhaustive extraction with an appropriate solvent. Methods for the determination of fat in cereals and of volatile oils in spices are well-known examples. In other cases however the constituents of the mixture have such similar solubility characteristics that exhaustive extraction results in the dissolution of the entire mixture. Clear-cut separations are not obtainable, and it is impossible to establish a value for the percentage of the more soluble fraction without resorting to purely arbitrary criteria for the amounts of solvent and sample used. The percentages of natural waxes which will dissolve in a certain solvent have been determined in this manner (1, 2).

The solubilities of natural waxes also have been expressed in terms of the grams of wax which will dissolve in 100 g. of the solvent (3). Although satisfactory for pure compounds, this expression of solubility is rather indefinite when applied to a mixture whose composition is changed during extraction. The solution in apparent equilibrium with undissolved wax may or may not be saturated with respect to every constituent of the mixture. The solubility thus obtained will be dependent upon the original amount of wax used.

The present paper describes a method which permits the calculation of the total amount of the more soluble fraction of a mixture from the amounts of material dissolved in each of several successive extractions.

An accurately weighed sample of the mixture is successively extracted with equal volumes of solvent to obtain a series of fractions. Following removal of the solvent by evaporation, each of the fractions is weighed. The total weight extracted, w, is then plotted against the number of extractions, n. The resulting curve is a section of a hyperbola, the shape of which has been determined by the solubility of the more soluble fraction of the mixture. The equation describing this curve is

$$w = \frac{n}{A + Bn} \tag{1}$$

where A and B are constants. Rearrangement of this equation shows that a straight line should be obtained by plotting n/w *vs.* n. The constant, B, is the slope of the line while A is its intercept on the n/w axis.

$$n/w = A + Bn \tag{2}$$

Multiplying through by w/n gives

$$1 = \frac{Aw}{n} + Bw \tag{3}$$

To determine the amount of the more soluble fraction present in the mixture, let the number of extractions approach infinity. The first term on the right-hand side of equation (3) approaches zero, and the maximum value of w equals 1/B. The amount of the more soluble fraction in the mixture is equal to the reciprocal of the slope of the linear graph.

Experimental

The solubility of sugar cane wax in ethanol was determined at 50°C. The extractor, designed to operate at constant temperature, is shown in Figure 1. It consists of a 250-ml. boiling flask fitted with a filter tube and a reflux condenser. The tube extends to within 1 mm. of the bottom of the flask, and the end is packed with a glass wool plug. Joints connecting the filter tube assembly to the flask and the condenser are made secure by springs.

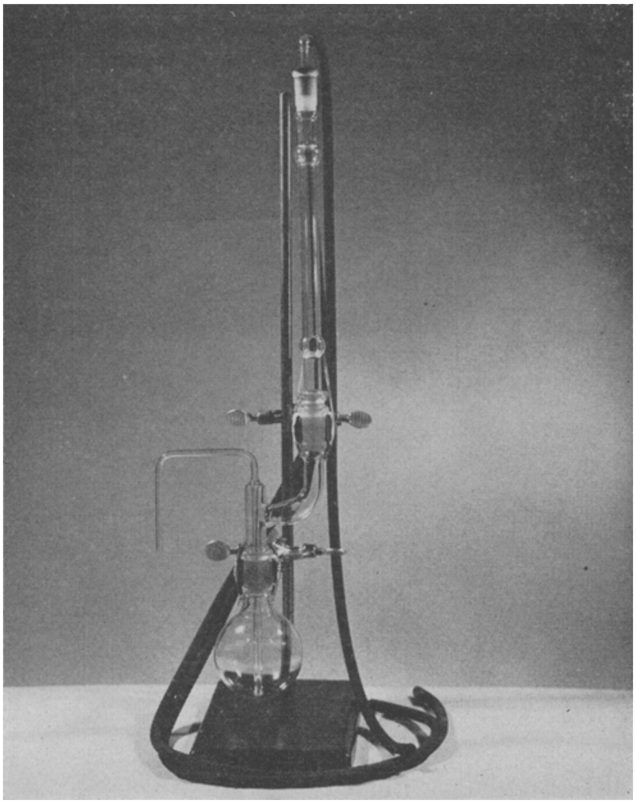

Fig. 1. Extraction apparatus.

The sugar cane wax was ground to pass a 40-mesh sieve. A 20-g. sample was accurately weighed into the flask, and the extraction tube was put in place. The flask was immersed in a constant temperature bath, and after a 10-min. warm-up period the designated quantity of ethanol which had been preheated to the bath temperature was added. The condenser was attached, and the contents of the flask were equilibrated for 30 min. with frequent shaking. The solution was then filtered off by applying nitrogen pressure to the open end of the condenser. It was necessary to warm the delivery tube with a heating lamp to prevent precipitation of some of the wax in the tube. The filtrate was caught in a small beaker, and the process was repeated. The solvent was evaporated from the samples of filtrates at 60°C., and the dried extracts were weighed.

Results

Data for two series of extractions are shown in Table I. The two series differ in that 25-ml. portions of ethanol were used in the first series while 50-ml. portions were used in the second. The calculated value of the weight of the soluble fraction appears opposite n = infinity. The percentages of the more soluble fraction are in agreement within three significant figures, indicating that the ratio of the amount of solute to solvent chosen for the extractions is not critical. The extraction curve for the first series is shown as the solid curve in Figure 2. The dashed curve represents the best hyperbola that can be drawn through the experimental points. It will be noted that the hyperbola exhibits a greater tendency to level off at the upper end than does the experimental curve. The latter will continue to remain above the hyperbola as n is further increased because the less soluble constituents are slowly dissolving and adding to the weight extracted. Since the shape of the hyperbola has been determined by the solubilities of the more soluble substances in the mixture, it approaches a limit which is less than the total weight of original sample.

TABLE I

Extraction of Sugar Cane Wax with Ethanol

Series	1	2
Weight of sample (g.)	19.3124	19.1062
Volume of solvent per extraction (ml.)	25	50
n	w (g.)	w (g.)
1	0.8049	1.4836
2	1.1915	2.2150
3	1.6912	2.7484
4	2 0664	3.1214
5	2.3991	3.4532
6	2.6666	3.7080
7	2.8921	3.9350
8	3.0965	4.1330
9	3.2677	4.3254
10	3.4426	4.5351
11	3.6273	4.6890
12	3.7615	4.8374
13	3.8960	....
14	4.0287	....
15	4.1482	....
∞	6.2618	6.1805
% alcohol-soluble fraction	32.42	32.35

n: number of extractions
w: weight of wax extracted

The straight line function for series 1 is shown in Figure 3. In practice the slopes were determined by least squares calculations instead of graphically. The plot of n/w *vs.* n should always be made to assure that the linear relationship holds. If the experimental points do not fall on a straight line, the extraction curve is not a hyperbola and this extrapolation procedure will not apply.

The method may be applied to the analysis of other types of extraction data. Extraction with chloroform in a Soxhlet extractor has been recommended by

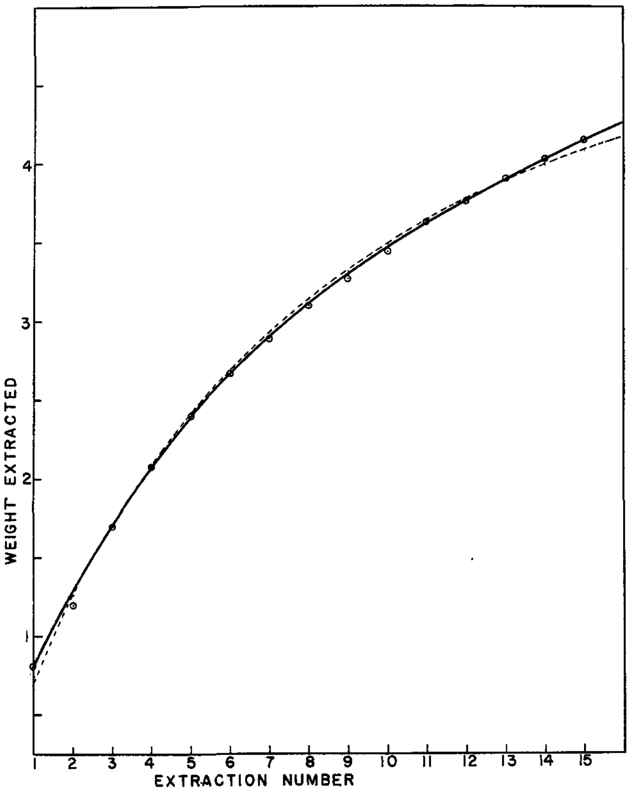

Fig. 2. Extraction curve for sugar cane wax.

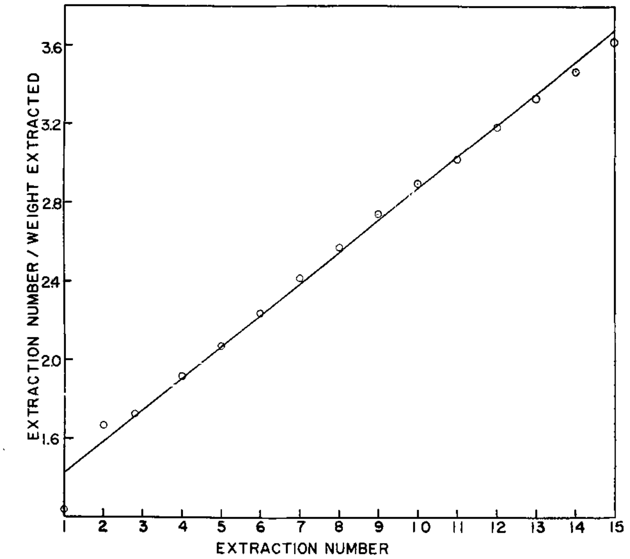

Fig. 3. Linear graph for determining the y-asymptote of curve in Figure 2.

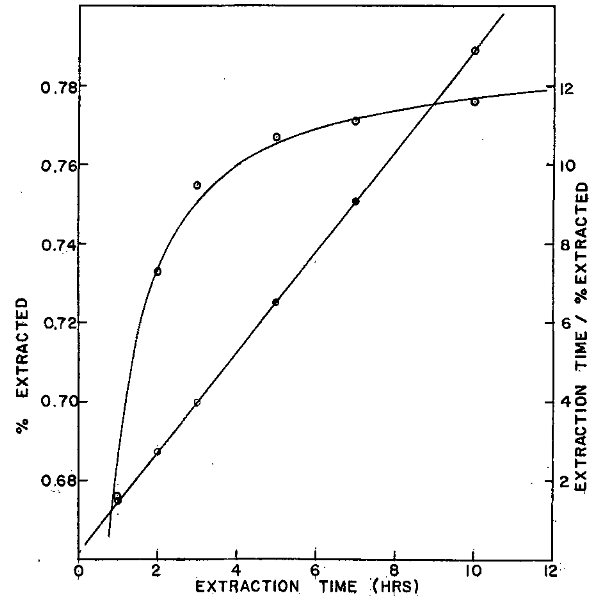

Fig. 4. Extraction curve and corresponding linear graph for extraction of Amerian cotton with hot chloroform.

Clifford *et al.* for the determination of fat, wax, and resin in cotton (4). After testing a variety of solvents, these workers correctly concluded that, although hot chloroform was best, no complete separation was possible. The question of how much soluble material remained unextracted naturally arises. Clifford's data include a tabulation of the percentage of sample extracted at various time-intervals. The data for the extraction of American cotton with hot chloroform are studied here. The percentage extracted is plotted against the extraction time in Figure 4. The experimental points are seen to lie very close to the best hyperbola which can be drawn through them. This hyperbola follows the equation, $\% = t/(1.269\ t + 0.1883)$. The straight-line function has been plotted in Figure 4 also. From this the total soluble material is found to amount to 0.788%. The longest extraction time reported in this series of extractions was 10 hrs., and in this time 0.776% of the sample had been extracted. The 10-hr. extraction thus removed 98.5% of the soluble material present in the cotton.

Summary

Successive extractions of mixtures are used to determine the percentage of the more soluble components present. A plot of the amount extracted *vs.* the extraction number results in a section of a hyperbola, which is then extrapolated to the limiting value. The solubility thus obtained is independent of arbitrary ratios of weights of solute to solvent. The method is applied to the determination of the alcohol-soluble fraction of sugar cane wax, and a laboratory extractor operating at constant temperature is described. Also the method may be used to analyze other extraction data, *e.g.*, extraction with the Soxhlet extractor, to determine the amount of soluble material left unextracted after a given time.

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ABSTRACTS . . . . R. A. REINERS, Editor

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• Fats and Oils

Isoöleic Acids. VI. Isoöleic Acids of Beef Liver and Goat Milk Fats. I. S. Shenolikar and M. R. Subbaram (Indian Council Med. Research, Coonoor). *J. Sci. Ind. Research* (India) **17C**, 207–8 (1958). The presence of Δ^8- through Δ^{13}-octadecenoic acids in the isoöleic acid from beef liver and goat milk fats is proved. (*C. A.* **53**, 11696)

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