SOME NEW DUCLAUX CONSTANTS*

G. R. YOHE and MYRA W. LANSFORD
State Geological Survey, Urbana

The Duclaux method for the recognition of volatile aliphatic acids[1, 2, 3, 4] is based upon the rate at which these acids distill from dilute aqueous solutions. The fraction of the total acidity of the original solution which comes over in each portion of distillate is characteristic of the acid being distilled and varies only slightly with the concentration of the solution and the presence of other volatile acids.

Duclaux used an original still charge of 110 ml. and collected ten 10 ml. fractions of distillate; the results were expressed as the cumulative percentages of the total acid distilled which were found in the successive fractions. He proposed that the values so obtained should serve for qualitative and quantitative analyses of a solution containing a single volatile acid or a mixture of two such acids.

The distillation method, as usually carried out, is empirical, and the values obtained vary with the size and form of the apparatus, with the method and rate of heating, and to some extent with the concentration of the original solution. Precision can be attained only by adherence to a standardized procedure. Data reported in the literature by different investigators show poor agreement because of differences in the procedures used[5]. Several authors have recommended that each analyst use his own equipment and conditions to redetermine the constants of the particular acids in which he is interested[6, 7].

The technique used in the present work is based on an adaptation of Duclaux's method for qualitative

TABLE 1.—DUCLAUX VALUES

Acid	I	II	III
Formic	3.6	4.0	4.5
Acetic	6.6	7.0	7.4
Propanoic	12.9	12.4	11.9
Butanoic	20.2	17.4	15.0
Methylpropanoic	29.0	21.5	16.3
Pentanoic	31.5	22.3	16.3
3–Methylbutanoic	35.9	23.9	16.2
dl–2–Methylbutanoic	36.6	24.0	16.2
Hexanoic	40.3	24.5	15.5
4–Methylpentanoic	42.4	25.2	15.4
2–Ethylbutanoic	46.5	25.5	14.0
Dimethylpropanoic	59.2	24.1	10.2

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[1] E. Duclaux: Annales de l'Ecole Normale supérieure 2, 270-90, 1865.

[2] E. Duclaux: Ann. chim. plys. [5], 2, 289-324, 1874.

[3] E. Duclaux: Ann. chim. phys. [6], 8, 542-63, 1886.

[4] E. Duclaux: Ann. inst. Pasteur, 9, 265-80, 1895.

[5] P. Jaulmes: J. chim. phys. 29, 403-17, 1932.

[6] E. P. Clark and F. Hillig: J. Assoc. Off. Agr. Chem. 21, 684-8, 1938.

[7] P. Fuchs: Chem.-Ztg. 68, 163-5, 1944.

analysis, believed by the writers to have been reported first by Kamm[8], which can be found in most textbooks on qualitative organic analysis. In this procedure, 100 ml. of solution of known total acidity is placed in the distilling flask and three 10 ml. fractions of distillate collected and titrated. If a single volatile acid is present, the titration data may serve to identify it.

This paper presents constants for four acids not included in the tables given in the qualitative organic textbooks, namely: dimethylpropanoic acid, dl-2-methylbutanoic acid, 4-methylpentanoic acid, and 2-ethylbutanoic acid.[9]

Data are reported in the literature for distillations by different techniques of aqueous solutions of 4-methylpentanoic acid[10, 11, 12], and of 2-thylbutanoic acid[13, 14, 15]. No comparable data have been found in the literature for dimethylpropanoic acid or dl-2-methylbutanoic acid.

Experimental

The apparatus consisted of a 300 ml. round-bottom flask, an acute-angle connecting tube, a 30 cm. water-cooled condenser, and a curved adapter; all connections were 24/40 standard taper glass joints. The distance from the base of the neck of the flask to the top of the connecting tube was 14 cm.; the internal diameter of the connecting tube was 1.7 cm. The condenser was set at 30° from the horizontal. The flask was heated with a spherical heating mantle connected through a variable transformer.

The acids used were obtained from various manufacturers. All were of reagent grade except the hexanoic acid, which was procured as technical grade and redistilled under reduced pressure, a one-degree cut being collected. All acids gave satisfactory neutralization equivalents, but no further tests of purity were made.

For each determination 150 ml. of a 0.2 percent (by weight) solution of the acid was prepared, and duplicate 10 ml. aliquots were titrated to determine total acidity. A 100 ml. portion of the solution was placed in the distilling flask, a boiling chip added, and the flask heated so that 5 to 6 minutes sufficed for the collection of each 10 ml. fraction of distillate. Three 10 ml. fractions were collected in 10 ml. graduated cylinders, and each was titrated. All titrations were made with standardized 0.02 N sodium hydroxide, using phenolphthalein as the indicator. The standard alkali was protected from the air, and the water used for all solutions was distilled water that had been boiled to remove carbon dioxide.

Results are expressed as percent of the total acidity of the 100 ml. of solution used. The values given in the table are averages of from three to six determinations. The average deviations of the individual determinations from the average figures reported in the table ranged from a

[8] O. Kamm, Qualitative organic analysis, John Wiley and Sons, New York, 1923, pp. 57-8, 139-40.
[9] Except for the common formic and acetic acids, compounds described in this paper are named in accordance with the systematic "International Union Rules"; cf. A. M. Patterson: J. Am. Chem. Soc. 55, 3905-25, 1933.
[10] O. Jensen: Z. Untersuch. Nahr. u. Genussm. 10, 265-83, 1905.
[11] D. C. Dyer: J. Biol. Chem. 28, 445-73, 1917.
[12] J. Reilly and W. J. Hickinbottom: Sci. Proc. Roy. Dublin Soc. 15, 513-38, 1919.
[13] H. D. Richmond: Analyst 42, 125-32, 1917.
[14] H. D. Richmond: Analyst 44, 255-74, 1919.
[15] A. I. Virtanen and L. Pulkki: J. Am. Chem. Soc. 50, 3138-51, 1928.

low of 0.1 percent for the III value for formic acid to a high of 2.1 percent for the II value for 2-ethylbutanoic acid. In general, greater deviations were encountered in the work with the higher molecular weight acids.

The values for hexanoic acid and the first seven acids listed in the table deviate by as much as 25 percent from the values for the same acids determined on 2 percent solutions with different apparatus and reported in qualitative organic textbooks[8, 16, 17, 18], although they indicate essentially the same relative order of volatility.

It can be seen from the table that although the values obtained in some cases are sufficiently characteristic to identify the acids, differentiation in other cases—e.g., between 3-methylbutanoic and dl-2-methylbutanoic acids — by Duclaux constants alone should not be attempted. Even where differences are somewhat greater, as with pentanoic and 3-methylbutanoic acids, differentiation would not be reliable unless data of carefully run controls on the known acids under the same distillation conditions were obtained for comparison.

[16] R. L. Shriner and R. C. Fuson: A systematic identification of organic compounds: John Wiley and Sons, New York, 3rd Ed., 1948, pp. 146-147.

[17] S. M. McElvain, The characterization of organic compounds: Macmillan Co., New York, 1945, pp. 140-1.

[18] F. Wild, Characterisation of pure organic compounds, Cambridge, University Press, 1948, pp. 156-7.