or phenylmethylene saligenin, forming white plates with a melting point of 54° and having the structure
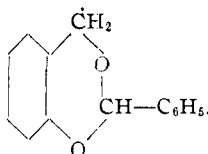
$$CH_2$$

CH—C_6H_5.

URBANA, ILLINOIS

RACEMIC ACID IN SOLUTION

By STUART WORTLEY PENNYCUICK

Several physical methods have been used to show the existence (or nonexistence) of the racemic molecule in solution. Some have given positive results, while others point to its complete breakdown into the two active forms.

Bruni and Padoa[1] from molecular-weight determinations conclude that racemic acid exists in solution in the presence of excess of one of the active forms. Kuster[2] by solubility determinations, and Dunstan and Thole[3] by a viscosity method find positive results. Stewart[4] by absorption spectra observations, and Rankin and Taylor[5] also find evidence of its existence. On the other hand specific gravity and heat of neutralization determinations,[6] as well as a rotatory dispersion method,[7] show no evidence of its independent existence.

An interfacial tension method as described in this paper leaves little doubt that the racemic molecule does exist in solution.

The interfacial tensions between aqueous solutions of (a) dextro tartaric, (b) levo tartaric, (c) racemic acid, and an inert liquid have been measured and the results compared. As a comparison of the interfacial tensions was aimed at, the drop method as developed by Tate,[8] Morgan[9] and co-workers, and Lohnstein[10] was adopted. The apparatus used was as

[1] Bruni and Padoa, Atti accad. Lincei., 11, 212 (1902).

[2] Kuster, Ber., 31, 1847 (1898).

[3] Dunstan and Thole, J. Chem. Soc., 93, 1815 (1908).

[4] Stewart, ibid., 91, 1537 (1907).

[5] Rankin and Taylor, Proc. Roy. Soc. Edinburgh, 27, 172 (1907).

[6] Jahn, Wied. Ann., 43, 306 (1891).

[7] Darmois, Trans. Faraday Soc., 10, 80 (1914).

[8] Tate, Phil. Mag., [iv] 27, 176 (1864).

[9] Morgan, THIS JOURNAL, 30, 360 (1908).

[10] Lohnstein, Z. physik. Chem., 64, 686 (1908).

described by Lewis.[11]   The interfacial tension, π, is taken as proportional
to the weight of a drop, *i. e.*,

$$\pi = K \times \text{wt. of 1 drop,} = \frac{K\ V\ \text{density}}{n}$$

where n is the number of drops for a given volume V.   As the same volume
is used in each case, and solutions of corresponding densities are taken,
$\pi \frown 1/n$.   It is therefore sufficient to read the drop number for fixed
volumes, and plot it against the concentrations.

Chemically pure *dextro* tartaric acid was recrystallized. Some of
it was converted into the racemic acid and the product recrystallized
thrice.   *Levo* tartaric acid was then made from racemic acid through
the cinchonine salt, and recrystallized until its rotation gave the maximum
value.   Thirty per cent. solutions of the *dextro* and *levo* acids were made
up and a 15% solution of the racemic acid.   Corresponding diluted so-
lutions were used, and the drop number given by toluene and by paraffin
obtained.   The absence of reaction between the oil and the acid was
shown by comparing the drop number given by the oil after shaking with
the acid, with the drop number given by the untreated oil.   No change
was observed.

TABLE I

Concentration of acid %	DROP NUMBER AGAINST TOLUENE			DROP NUMBER AGAINST PARAFFIN		
	Dextro acid	*Levo* acid	Racemic acid	*Dextro* acid	*Levo* acid	Racemic acid
. .	171	173	172	233	235	233
2.5	183	186	195	260	257	289
5	200	204	220	286	285	338
7.5	216	211	242	310	314	390
10	233	234	264	339	338	427
12.5	253	251	288	359	366	470
15	274	271	308	394	385	522
22.5	330	. . .	. . .	. . .	. . .	. . .
30	386	. . .	. . .	. . .	. . .	. . .

If the interfacial tension of such solutions be measured against an opti-
cally active liquid an interesting question arises.   Certain optically active
solutions of enzymes have a marked selective action on enantiomorphs,
attacking one form strongly and the other form very slightly.   Numerous
glucosides are selectively hydrolyzed in this way; *e. g.*, α-methyl glucoside
and α-methyl galactoside by maltase and not by emulsin, while the enantio-
morphs are hydrolyzed by emulsin and not by maltase.   Bayliss has
shown that in nearly every case examined both forms are actually attacked.
No satisfactory physical or chemical explanation has been put forward
for this selective action, and neither a vitalistic theory nor a "lock and

[11] Lewis, *Phil. Mag.*, **1908.**

key" explanation goes very far. The suggestion has been put forward
by Dr. Denham (and in fact it was this suggestion that started
the present work) that the selective action might be due to selective
adsorption of the optically active substrate upon the surface of the opti-
cally active catalyst. Evidence concerning such selective adsorption
might possibly be afforded by determing the interfacial tensions of opti-
cally active solutions against an optically active oil, or against an oil
rendered optically active by such a solute as camphor. The difficulty
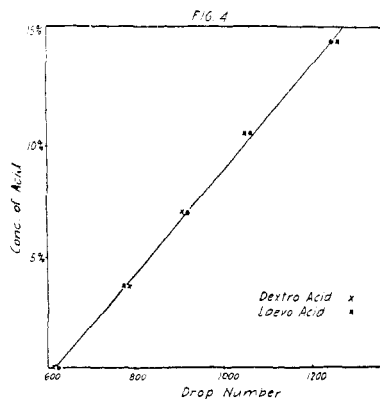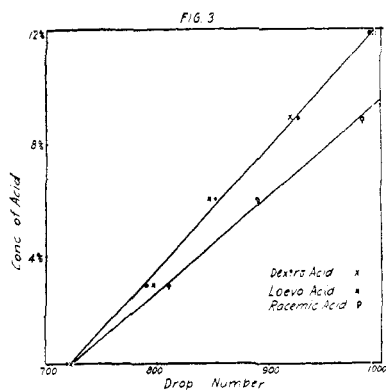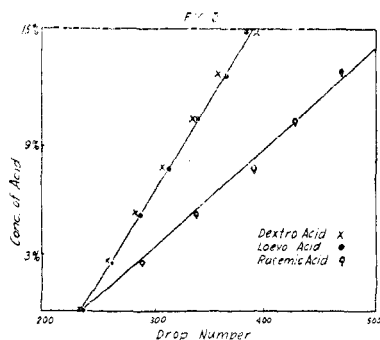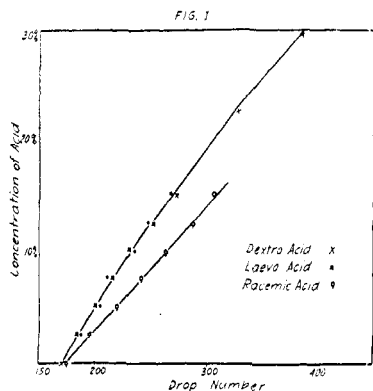
of procuring in sufficient quantity an oil which possessed at the same
time the desired degree of optical activity and yet did not dissolve in,
nor react chemically with, the aqueous solution of the chosen active
solute, compelled the author to use as the active oil a solution of camphor
in benzene. The absence of reaction between this active oil and the aqueous
solution of the active acid was again tested by taking the drop number of
this oil before and after shaking with an aqueous solution of d-tartaric acid.
The values recorded were identical.

Drop numbers of the *dextro, levo* tartaric and racemic acids were then

taken against the camphor-benzene solution,[12] and also those of *dextro* and *levo* camphor-sulfonic acids against the camphor-benzene solution.

TABLE II

DROP NUMBER AGAINST A SOLUTION OF CAMPHOR IN BENZENE

Conc. of acid in water %	d-Tartaric	l-Tartaric	Racemic	Conc. of acid in water %	d-Camphor-sulfonic acid	l-Camphor-sulfonic acid
		17%			26%	
..	720	724	728	..	613	619
3	796	791	810	3.7	795	777
6	846	852	891	7	915	916
9	920	925	983	10.5	1056	1059
10.4	...	...	1015	14.7	1257	1253
12	994	990	..	..	..	..

Conclusion

The results show that there is no measurable difference in interfacial tension, against the several liquids, between the *dextro* and the *levo* substances chosen, indicating that there is no selective absorption of such enantiomorphs, which are remarkable for their similarity of physical properties.

The divergence of the curve for either of the active tartaric acids from that for the racemic acid (see Figs. 1, 2 and 3) appears to admit of only one explanation, the existence in solution of the racemic acid molecule. As the dilution increases, the curves indicate an increasing "dissociation" of the racemic acid into the *d* and *l* forms.

I am indebted to Professor H. G. Denham, now of the University of Cape Town, South Africa, for his initial suggestion and for his advice during the progress of this work.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

C₁₈ FATTY ACIDS. IV. A REARRANGEMENT OF THE BENZILIC ACID TYPE IN THE ALIPHATIC SERIES

BY BEN H. NICOLET AND ALFRED E. JURIST[1]

Some time ago Le Sueur[2] described the fusion of 9,10-dihydroxystearic acid (I) with potassium hydroxide. The principal reaction was shown to be the formation of α-hydroxy-α-octyl-sebacic acid (II), resembling benzilic acid in structure, and the evolution of hydrogen, though the considerable amount of material not accounted for indicated that side reactions were also taking place.

[12] The author is indebted to Professor Read, University of Sydney, for the supply of camphor-sulfonic acids.

[1] The material here presented was used by Alfred E. Jurist in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

[2] Le Sueur, *J. Chem. Soc.*, **79**, 1313 (1901).