group, the halogen substituents appear to produce the greatest discrepancies between the observed and calculated values.

Accumulation of Negative Groups.—When there is an accumulation of negative groups in the molecule, particularly if attached to adjacent carbon atoms, the calculated value of I is considerably more than the observed value. This fact, as shown by Table III, indicates that an additional negative "strain-constant" is required. Better data on such compounds and further study are required before it may be determined whether adequate "strain-constants" can be derived.

TABLE III

ACCUMULATION OF NEGATIVE GROUPS

Compound	I, obsd.	I, calcd.	Diff.
Chloroform	221–226	232.9	+ 7
Carbon tetrachloride	278–282	303.2	+23
Tetrachloroethylene	296–299	324.9	+27
1,1,2,2-Tetrachloroethane	316–318	345.8	+29
Trichloroethylene	250	267.6	+18
Pentachloroethane	366	403.1	+37
Dibromomethane	212	213.6	..
Bromoform	264	289.9	+16
Ethylene bromide	257–259	269.2	+11
1,2-Dibromopropane	311	324.8	+14

Summary

1. An equation relating viscosity and density, $\log_{10}(\log_{10}\eta) = md - 2.9$, is found to fit the data on 117 organic liquids.

2. The viscosity–density constant, m, is characteristic of each liquid and when multiplied by molecular weight becomes a constitutive property, I, of each compound.

3. Values of atomic and structural constants are derived from which the viscosity–constitutional constant, I, may be calculated.

4. Comparison of the observed and calculated values of I for 117 organic liquids indicates, in nearly all cases, errors of less than 1%.

NEW HAVEN, CONN. RECEIVED NOVEMBER 10, 1937

α-Aryl-β-dialkylaminoalkyl Ureas as Local Anesthetics

BY HENRY WENKER

Since compounds which contain an aromatic nucleus combined, by means of an electronegative group, with a dialkylaminoalkyl radical, often possess local anesthetic properties, the preparation of some ureas to which the above description applies, seemed of interest. Only one compound of this class has been described hitherto.[1]

The ureas under consideration were prepared by the action of an aryl isocyanate with an *as*-dialkyl alkylenediamine. The isocyanates used were phenyl-, *o*-methoxyphenyl-, *p*-ethoxyphenyl isocyanate and phenyl isothiocyanate; the amines used were 1-piperidino-2-aminopropane and 1-di-*n*-butylamino-2-aminopropane. The ureas, as far as they were obtained in crystalline form, are described in the table.

Experimental

Piperidine and di-*n*-butylamine, respectively, were combined in the usual manner with propylene oxide. Of the resulting amino alcohols the former is known;[2] the latter, obtained in 84% yield, forms a colorless liquid boiling at 130° (15 mm.).

Anal. Calcd. for $C_{11}H_{25}NO$: N, 7.5. Found: N, 7.4.

The hydrochlorides of the amino alcohols were allowed to react with a 50% excess of thionyl chloride for twenty-four hours at room temperature and the excess of thionyl chloride was then removed by gentle heating *in vacuo*. The crude hydrochlorides of the β-chloropropyl bases were used for the following reaction; a sample of the well-crystallized N-(β-chloropropyl)-piperidine hydrochloride, however, was crystallized from amyl acetate. It forms long needles melting at 204°.

Anal. Calcd. for $C_8H_{17}NCl_2$: Cl, 36.0. Found: Cl, 36.2.

No.	Urea	Formula	M. p., °C.	N, % Calcd.	N, % Found
1	α-Phenyl-β-(1-piperidinopropyl-2)	$C_{15}H_{23}ON_3$	149	16.1	16.1
2	α-(*o*-Methoxyphenyl)-β-(1-piperidinopropyl-2)	$C_{16}H_{25}O_2N_3$	135	14.4	14.6
3	α-(*p*-Ethoxyphenyl)-β-(1-piperidinopropyl-2)	$C_{17}H_{27}O_2N_3$	124	13.8	13.6
4	α-Phenyl-β-(1-piperidinopropyl-2)-thio	$C_{15}H_{23}SN_3$	123	15.2	15.2
5	α-Phenyl-β-(1-di-*n*-butylaminopropyl-2)	$C_{18}H_{31}ON_3$	113	13.8	13.9
6	α-(*o*-Methoxyphenyl)-β-(1-di-*n*-butylaminopropyl-2)	$C_{19}H_{33}O_2N_3$	94[a]	12.2	12.1

[a] The melting point may be low, as the compound crystallized difficultly.

(1) Ristenpart, *Ber.*, **29**, 2527 (1896).

(2) German Patent 547,174 (1927).

The hydrochloride of β-chloropropyl-di-*n*-butylamine did not crystallize and was not analyzed. No attempt was made to isolate the free bases, since halogen amines of this type are known to be unstable except in form of their salts.

One mole of each salt was added to a solution of 10 moles of ammonia in methanol. After standing for four days at 60°, the charges were neutralized with aqueous hydrochloric acid, methanol removed by distillation, the bases separated with sodium hydroxide, dissolved in ether, dried with sodium sulfate and fractionated. Both are colorless liquids. 1-Piperidino-2-aminopropane boils at 193–194°. The yield was 22%.

Anal. Calcd. for $C_8H_{18}N_2$: N, 19.7. Found: N, 19.5.

1-Di-*n*-butylamino-2-aminopropane, obtained in 32% yield, boils at 132° (15 mm.).

Anal. Calcd. for $C_{11}H_{26}N_2$: N, 15.1. Found: N, 14.9.

Preparation of the ureas: molar quantities of isocyanate and diamine were combined in toluene solution at room temperature; after diluting with ether, the urea was extracted with dilute hydrochloric acid, precipitated with sodium carbonate and crystallized from dilute methanol. All of the ureas form white crystals, soluble in alcohol and in ether. They are practically insoluble in water, but dissolve readily in the theoretical amount of hydrochloric acid with neutral reaction. Solutions of the hydrochlorides of ureas 5 and 6 produce local anesthesia on the tongue.

Summary

The analogy of α-aryl-β-dialkylaminoalkyl ureas with known local anesthetics has been pointed out and five ureas and one thiourea of this type have been prepared. Two of these compounds are local anesthetics.

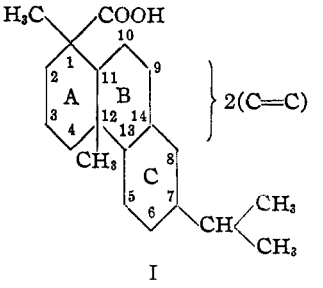
ELIZABETH, N. J. RECEIVED OCTOBER 19, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Concerning Dehydroabietic Acid and the Structure of Pine Resin Acids

BY LOUIS F. FIESER AND WILLIAM P. CAMPBELL[1]

The chief purpose in undertaking the present work on abietic acid was to explore the possibility of utilizing this abundantly available hydrophenanthrene derivative as a starting material for the preparation of compounds related sufficiently closely in structure to various naturally occurring compounds of the phenanthrene group to give promise of simulating their physiological actions. The independent work of Vocke,[2] Ruzicka,[3] and R. D. Haworth[4] in 1932 established beyond reasonable doubt[5] the skeletal structure I for abietic acid, and the only remaining point of uncertainty is with respect to the location of the two nuclear double bonds. With a center of unsaturation in one part of the molecule and an acidic group in a terminal ring, abietic acid offers the possibility for various chemical transformations, and it was our plan to attempt to aromatize ring C, introduce a phenolic hydroxyl group into this ring, and, in one series of experiments, transform the carboxyl group into an alcoholic group. An alcohol-phenol of the type envisioned might share some of the physiological properties of oestradiol, and the elaboration of the original carboxyl group to a nitrogen-containing side chain would provide an approach to substances of morphine-like structure. The first objective has been realized, and the present paper reports the preparation of a derivative of abietic acid containing one aromatic nucleus.



I

Before describing the new compound, certain inferences may be presented regarding the positions of the double bonds in the resin acids. When Ruzicka, Ankersmit and Frank[6] first noted that abietic acid can be caused to add maleic anhydride, the observation seemed to indicate that

(1) Squibb Research Fellow.

(2) Vocke, *Ann.*, **497**, 247 (1932). Confirmatory synthetic evidence has been reported recently by Rydon, *J. Chem. Soc.*, 257 (1937).

(3) Ruzicka, de Graaff and H. J. Müller, *Helv. Chim. Acta*, **15**, 1300 (1932).

(4) R. D. Haworth, *J. Chem. Soc.*, 2717 (1932).

(5) Clemo and Dickenson, *ibid.*, 255 (1937), suggested the possibility that an original *gem*-methyl-ethyl group at position 7 is transformed into an isopropyl group in the course of the dehydrogenation of abietic acid. Their model experiments, however, lent no support to this view, and the isolation of isobutyric acid as an oxidation product of abietic acid (see discussion below) provides a positive proof of the presence of an isopropyl group.

(6) Ruzicka, Ankersmit and Frank, *Helv. Chim. Acta*, **15**, 1289 (1932).