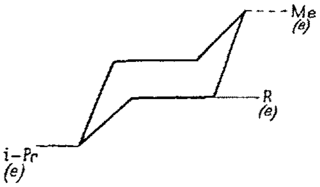
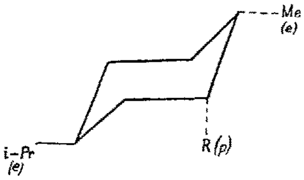
Brèves communications - Kurze Mitteilungen
Brevi comunicazioni - Brief Reports

The Conformation of Carvomenthols

The recently elaborated method of conformational analysis[1] can be used for determining the stereochemistry of carvomenthols and carvomenthylamines. READ and JOHNSTON[2] have shown that an equilibrium mixture of (−)-carvomenthone and (−)-isocarvomenthone contains 79% of the former. Carvomenthone being the more stable epimer should have both the methyl and isopropyl groups linked by equatorial bonds while isocarvomenthone should have the isopropyl group equatorially linked and the methyl group polar linked. The main reaction products in the sodium and alcohol reduction of (−)-carvomenthone and (−)-carvomenthoneoxime are (+)-carvomenthol (I) and (+)-carvomenthylamine (II) respectively. It has been observed[3] that this type of reduction leads to the thermodynamically more stable epimer of an alcohol or an amine. All the substituents in I and II are, therefore, equatorially bonded. Neocarvomenthol and neocarvomenthylamine—the corresponding epimers, should be represented by the conformations III and IV in which the hydroxy and amino groups are polar linked. In the adjoining figures the unbroken lines indicate constituents above the puckered plane of the ring and broken lines those below the plane and (*p*) and (*e*) represent polar and equatorial bonds respectively.



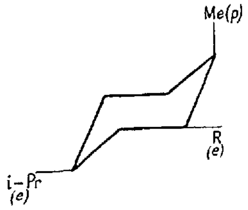
I $R = \mathrm{OH}$
II $R = \mathrm{NH_2}$



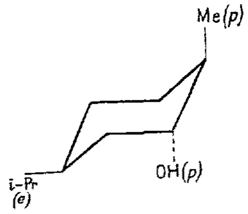
III $R = \mathrm{OH}$
IV $R = \mathrm{NH_2}$

The sodium and alcohol reduction of (−)-isocarvomenthoneoxime leads predominantly to (−)-isocarvomenthylamine (VI). The amino and the isopropyl groups are, therefore, equatorial and the methyl group polar in VI.

A study of the data on the reaction of nitrous acid with menthylamines and decalylamines shows that if the amino group be equatorially linked, the reaction product is mainly the corresponding alcohol with the hydroxy group equatorial but if the amino group be polar, considerable amounts of unsaturated compounds are produced along with a mixture of both epimeric forms of the alcohol[1]. Since the interaction of nitrous acid with isocarvomenthylamine (VI) affords (−)-isocarvomenthol and very little terpene, we can assign the conformation V to isocarvomenthol and VII to its epimer—neoisocarvomenthol.



V $R = \mathrm{OH}$
VI $R = \mathrm{NH_2}$



VII

The observation that on treatment with nitrous acid (+)-carvomenthylamine (II) yields mainly (+)-carvomenthol but (−)-neocarvomenthylamine (IV) affords mostly terpenes and a small amount of a mixture of carvomenthol (I) and neocarvomenthol (III), constitutes evidence in favour of the conformations I, II, III, and IV. Further, these conformations lead to configurations for carvomenthol, carvomenthylamine, neocarvomenthol and neocarvomenthylamine which are identical with those deduced by READ and his co-workers[2] on the basis of completely different considerations.

The configurations of isocarvomenthol and isocarvomenthylamine do not seem to have been determined previously. Evidence for the correctness of the conformations V and VI is provided by the observation that V is esterified preferentially when a mixture of III and V is treated with an insufficient amount of p-nitrobenzoyl chloride. The hydroxy group in V which is equatorially bonded is expected to react faster than the polar linked

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[1] D. H. R. BARTON, Exper. *6*, 316 (1950). – D. H. R. BARTON and W. J. ROSENFELDER, J. Chem. Soc. *1951*, 1048. – W. S. JOHNSON, Exper. *7*, 315 (1951).

[2] J. READ and R. G. JOHNSTON, J. Chem. Soc. *1934*, 226; *1935*, 1138.

[3] W. HÜCKEL, E. KAMENZ, A. GROSS, and W. TAPPE, Ann. Chem. *533*, 1 (1938).

[1] To be discussed in a separate communication.

[2] N. L. McNIVEN and J. READ, J. Chem. Soc. *1952*, 153.

hydroxy group in III because an equatorial substituent is sterically less hindered than the same substituent at the same position linked through a polar bond[1].

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Zusammenfassung

Die «Conformation» aller Carvomenthole und Carvomenthylamine wurde auf der Grundlage der Vorstellung von polaren und äquatorialen Bindungen abgeleitet. Die Konfiguration von Carvomenthol, Neocarvomenthol, Carvomenthylamin und Neocarvomenthylamin, die aus ihrer «Conformation» folgt, ist identisch mit der Konfiguration, die von Read und Mitarbeitern hauptsächlich auf der Grundlage der von-Auwersschen Regel vorgeschlagen wurde. Die «Conformation» des Isocarvomenthols und des Isocarvomenthylamins lässt erkennen, dass sich alle Substituenten in diesen beiden Verbindungen in *Cis*-Stellung befinden.

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[1] D. H. R. Barton, Exper. *6*, 316 (1950). - D. H. R. Barton and W. J. Rosenfelder, J. Chem. Soc. *1951*, 1048.

A Study of the Clay Fraction of Egyptian Soils

The soil of Egypt is formed from the Nile deposits resulting from the disintegration of the igneous rocks of the Ethiopian plateau due to the chemical and physical weathering factors.

The clay fraction is the active part of the solis. The properties of the different types of clay depend upon the following characteristics: (a) The size of the particles, (b) the chemical nature of the clay, i.e. its exchange reaction and the water-binding capacity, etc., and (c) the plate-like structure of the particles.

Material: The sample for this study was taken from the Faculty of Agriculture's farm situated at 30° 2′ N and 31° 13′ E in Giza about 0·8 km west of the River Nile.

Table I

The chemical analysis of H-clay, oven dry basis

Constituents	Percentage
SiO_2	56·52
Al_2O_3	25·32
Fe_2O_3	14·00
CaO	0·74
MgO	1·87
K_2O	1·60
Na_2O	1·48

The sample was placed in a high cylinder and a litre of distilled water was added. After the soil became thoroughly wetted, the mixture vigorously stirred and left for sedimentation. Afterwards, a syphon under the surface was inserted and the suspension was removed. The fine particles were leached with $^{n}/_{250}$ HCl several times to replace all the alkaline and alkaline earth ions with H-ions and consequently a pure clay sample was obtained. The sample was washed Cl-free with water and then electrodialysed.

Results: (1) *The chemical analysis.* – The chemical analysis of the H-clay produced was carried out by the fussion method[1]. The Table I gives the results.

The evaluation of the chemical analysis is very difficult owing to the presence of an amorphous part[2] mixed with the crystalline fraction. Also the continuous washing with water and HCl strongly reduced the alkaline content.

(2) *Exchange capacity.* – The exchange capacity of the clay was determined with $Ba(OH)_2$ after Wiklander[3]. 2–3 g of the clay were suspended in water and then 10 ml of $Ba(OH)_2$ were added. After equilibrium was reached, the Ba-clay was mixed with ion exchanger JR. amberlite 120 and the Ba-ion adsorbed was estimated as $BaSO_4$. Table II shows the absorbed milliequivalent Ba-ion.

Table II

Milliliter Ba-adsorbed/g H-clay air dried (9·98% H_2O)

Initial concentration in m.e.	m.e. adsorbed Ba^{++}
5·00	1·14
10·00	1·18

(3) *The electron micrograph*[4]. – As the scattering in the electron microscope is proportional to the thickness and density of the sample exposed, it is necessary that the particles should be very fine and the film extremely thin and homogeneous.

For this study, the finest fraction was obtained as follows: lg of H-clay was suspended in water, peptized with NH_4OH[5] and then left some days for sedimentation. The sample for the electron micrograph was made by allowing a drop of the suspension to evaporate on a thin collodion membrane which was previously dried.

The electron micrograph shows an aggregated material with plate-like structure. The sample is made up of very thin plates mixed with thicker units. Fine particles of quartz are also easily seen together with the thicker undispersed units, which agree with Eitel's observations[6]. The electron micrograph classifies the Egyptian alluvium clay mineral with the illitic group.

(4) *X-ray analysis.* – Two powder diagrams[7] have been taken according to the Debye-Scherrer method with Fe-radiation $\lambda = 1{\cdot}93239$ Å, in a camera diameter of 114·4 mm.

The first diagram represents the original clay before leaching with diluted HCl, and the second one shows that of the H-clay. Table III gives the glancing angles and lattice-spacings of both samples.

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[1] F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, vol. 2 (John Wiley Inc., New York, 1945).

[2] H. Hamdi and M. Naga, Schweiz. Min. Petrogr. Mitt. *29*, 537 (1949).

[3] L. Wiklander, Anal. roy. Agr. College Sweden *16*, 670 (1949).

[4] The micrograph was taken in the Plant Physiology Department of E.T.H. Zurich. We express our thanks to Ing. R. Iberg for his kind help.

[5] C. W. Correns and W. Scott, Koll.-Z. *61*, 68 (1932) - C.W. Correns, Zbl. Min. Abt. A *321* (1934).

[6] W. Eitel, H. Müller, and G. Radczewsky, BDK. Ges. *20*, 165 (1939).

[7] The powder diagrams have been taken in the Min. and Petrogr. Institut of E.T.H. Zurich. We are indebted to Dr. W. Epprecht for his help.