hydrochloric acid and extracting with ether. The acid is easily soluble in ether and in benzene, almost insoluble in ligroin. It melts at 73–74°. The acid appears to decompose and become semisolid on standing. Perhaps for this reason the analyses, especially the nitrogen determinations are not very satisfactory, but when these are taken with the titration values and the composition of the barium salt the formula assigned to the acid seems to be established.

Calculated for $C_6H_9O_4N$: C, 45.2 ; H, 5.66 ; N, 8.80.
Found: C, 45.6, 45.8, 45.8; H, 5.9, 6.35, 6.4; N, 7.8, 7.5.

Titration with 0.1 *N* sodium hydroxide gave a molecular weight of 162.9 and 163.0; with barium hydroxide 166. Theory 159.

The Barium Salt, $(C_6H_8NO_4)_3Ba.\ 2^1/_2\ H_2O$ was analyzed completely because of the apparent instability of the acid. For the carbon determinations it was mixed with potassium dichromate to expel the carbon dioxide from the barium carbonate.

Calculated for $(C_8H_9NO_4)_2Ba.2\ 1/2\ H_2O$: C, 28.9 ; H, 4.2.
Found: C, 29.2, 29.0; H, 4.8, 44.7.

The anhydrous salt gave 6.38 per cent. N; calculated 6.14.

The salt lost 9.73 per cent. water at 80°. Calculated for 2 1/2 H_2O, 9.04 per cent. The anhydrous salt gave 30.34 and 30.27 per cent. Ba; calculated 30.30.

From lack of time and the difficulty of preparing the material we have been unable to undertake experiments which might throw light on the structure of the acid.

URBANA, ILL.

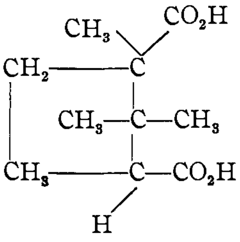
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. VII. DERIVATIVES OF ISOCAMPHORIC ACID; *l*-DIHYDROHYDROXYCAMPHOLYTIC ACID.

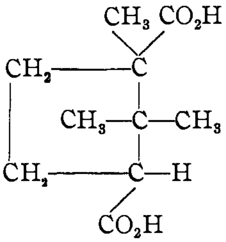
BY WILLIAM A. NOYES AND LUTHER KNIGHT.

Received October 13, 1910.

It is generally assumed that *d*-camphoric acid and *l*-isocamphoric acid, which, as Aschan has shown, are each convertible into the other, are stereomers and differ only in that one is a *cis* and the other a *trans* form. This may be expressed by the following formulas:



d-Camphoric acid.



l-Isocamphoric acid.

Since methyl groups are known to shift from one carbon atom to another at much lower temperatures and under the influence of much less vigorous agents than those used to convert camphoric to isocamphoric acid the evidence for the structure of the latter does not appear to be altogether conclusive and it seemed to be of interest to obtain further evidence on this point. The study of the subject is far from complete but we have already obtained interesting and unexpected results.

Preparation of Isocamphoric Acid.—The method of preparing *l*-isocamphoric acid by heating *d*-camphoric acid with a mixture of hydrochloric and acetic acids[1] has been modified by largely increasing the proportion of camphoric acid used and also decreasing the amount of hydrochloric acid. The tubes are charged with 50 grams of *d*-camphoric acid, 25 cc. of glacial acetic acid and 2 cc. of concentrated hydrochloric acid (1.19). After sealing, the tubes are heated for ten hours at 170–180°. On account of the larger amount of acetic acid used the contents of the tubes are liquid after cooling. The acetic and hydrochloric acids are completely expelled by evaporation on the water bath and the residue after powdering finely is allowed to stand for an hour or longer with one-fourth of its weight of acetyl chloride (instead of the very large excess used by Aschan). The mixture is then treated with water and acid sodium carbonate, which dissolves the isocamphoric acid leaving the *d*-camphoric anhydride dissolved. From the filtrate the *l*-isocamphoric acid is precipitated by hydrochloric acid. In this manner 100 grams of the *d*-camphoric acid gave 37 grams of an acid containing 95.5 per cent. of isocamphoric acid as shown by the rotation. The camphoric anhydride which is recovered may be used for treatment with acetic and hydrochloric acids again, after crystallizing it from alcohol, and in this manner the conversion to isocamphoric acid may finally be made almost quantitative. The isocamphoric acid is easily purified by crystallization, best by dissolving it in a small amount of strong alcohol, adding 3 or 4 volumes of hot water, and allowing the solution to cool while exposed to the air, allowing a part of the alcohol to evaporate. The purified acid gave in a 10 per cent. alcoholic solution a rotation of $(\alpha)_D = -47.1°$, Aschan gives $-47.1°$.

α-Monomethyl Ester of l-Isocamphoric Acid.[2]—As with *d*-camphoric acid and its derivatives the secondary carboxyl of *l*-isocamphoric acid is much more easily esterified than the tertiary.[3] It is, accordingly easy to select conditions which will give chiefly the α-acid ester.

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[1] Aschan, *Ber.*, 27, 2005.

[2] Assuming that isocamphoric acid is stereomeric with camphoric acid, the secondary carboxyl is called α and the tertiary carboxyl β. See Noyes, *Am. Chem. J.*, 16, 500; 18, 686.

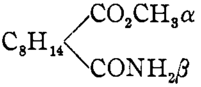
[3] Noyes, *Am. Chem. J.*, 18, 686.

One hundred grams of isocamphoric acid, 400 cc. of methyl alcohol and 40 cc. of concentrated sulphuric acid were boiled for 20 minutes with a return condenser. The methyl alcohol was then distilled away under diminished pressure and the mixed esters which were precipitated with water were shaken with a strong solution of sodium carbonate which dissolved the acid ester. The neutral ester, which is always formed and which may become the principal product if the boiling is too long continued, was taken up with ether and distilled under diminished pressure. The acid ester was precipitated on adding hydrochloric acid to the sodium carbonate solution. The yield of acid ester may reach 95 per cent. of the theory.

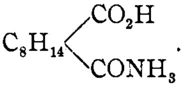
The Dimethyl Ester of Isocamphoric Acid, $C_2H_{14}(CO_2CH_3)_2$, boils at 146° under 27 mm. pressure and has a specific gravity of 1.073 at 20° and 1.069 at 25°. Its specific rotation, $(\alpha)_D^{21°} = —65.2°$. In 10 per cent. alcoholic solution $(\alpha)_D = —63.6°$.

The α-Monomethyl Isocamphoric Ester prepared as described above was crystallized from petroleum ether. It crystallizes in needles which melt at 88°. In 10 per cent. alcoholic solution $(\alpha)_D = —57.9°$.

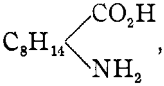
0.2340 g. required for neutralization 10.85 cc. and 0.4640 g. required 21.66 cc. 0.1 *N* KOH; calculated, 10.92 and 21.69 cc.

Amide of the α-Monomethyl Ester of Isocamphoric Acid,  $C_8H_{14}\left\langle\begin{array}{l}CO_2CH_3\alpha\\CONH_2\beta\end{array}\right.$ —The acid methyl ester last described was mixed in a distilling bulb with an equal weight of phosphorus pentachloride, the mixture being cooled when more than a few grams are used. When the reaction is complete the phosphorus oxychloride is distilled away as rapidly and under as low a pressure as possible. The acid chloride is then poured carefully into a slight excess of ammonia (0.90), the latter being thoroughly cooled with ice or a freezing mixture. The amide obtained was crystallized from dilute alcohol. It crystallizes in plates on spontaneous evaporation of the alcohol. It melts at 157°. In 10 per cent. alcoholic solution $(\alpha)_D = —60.05°$.

The analysis gave 6.68 per cent. N; calculated, 6.57 per cent.

β-Isocamphoramidic Acid,  $C_8H_{14}\left\langle\begin{array}{l}CO_2H\\CONH_3\end{array}\right.$.—The amide of the monomethyl ester of isocamphoric acid was dissolved in alcohol, 10 per cent. in excess of one molecule of sodium hydroxide in a 30 per cent. solution was added and the mixture was heated for an hour or two on the water bath. Under these conditions the methyl ester is completely saponified while the amide group is scarcely affected. After removal of the alcohol by evaporation the β-isocamphoramidic acid was precipitated by hydrochloric acid and crystallized from dilute alcohol. It crystallizes in needles which melt at 165–166°.

The analyses gave 7.07 and 7.11 per cent. N; calculated 7.03 per cent. 0.0485 g. took 2.3 cc. 0.1 *N* NaOH; calculated, 2.35 cc.



Isodihydroaminocampholytic Acid, $C_8H_{14}\left\langle\begin{matrix}CO_2H\\NH_2\end{matrix}\right.$, was prepared from the isocamphoramidic by treating a solution of its sodium salt with a solution of sodium hypobromite.[1] The latter solution was prepared by aspirating the vapor of the measured or weighed amount of bromine through a 10 per cent. solution of sodium hydroxide.[2]

The Hydrochloride, $C_8H_{14}CO_2HNH_2.HCl$, was obtained by evaporating the acid solution to dryness and extracting the residue with strong alcohol. It is very easily soluble and crystallizes from concentrated solutions in needles. These do not melt at 250°.

0.0957 g. required 4.4 cc. 0.1 *N* $AgNO_3$; calculated, 4.5 cc.

The Lead Salt, $(C_8H_{14}NH_2CO_2)_2Pb$ was prepared by precipitation from an acetic acid solution and purified by washing with hot water in which it is almost insoluble.

The analysis gave 38.8 and 37.4 per cent. Pb; calculated, 37.8 per cent.

The Free Isodihydroaminocampholytic Acid (not very pure) melts at 225–227°. When heated to 250 or 300° it gives an anhydride and the latter gives a nitroso compound which melted at 194° when freshly prepared but at 174–175° after standing overnight. These will be studied further.

When a solution of the hydrochloride of isodihydroaminocampholytic acid is treated with the calculated amount of a 20 per cent. solution of sodium nitrite introduced with a pipet beneath the former so that the two solutions mix by diffusion there are formed, apparently, a hydrocarbon, a lactone, *d*-campholytic acid and *l*-dihydrohydroxycampholytic acid. Only the last has been obtained in a fairly pure condition and fully identified.

The products at first obtained were taken up with ether and after removal of the latter the hydrocarbon, lactone and campholytic acid were distilled with steam. The lactone and campholytic acid were separated by means of sodium carbonate. The rotation of the campholytic acid finally obtained was +46° and it gives by titration results agreeing closely with the theory, but, in consideration of the small amount thus far obtained and of the fact that the rotation is not, as it should be, the same, though of sign opposit to that of *l*-campholytic acid[3] there is still some slight doubt as to the nature of the compound.

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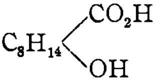
[1] Noyes, *Am. Chem. J.*, **16**, 503.

[2] Dehn, THIS JOURNAL, **31**, 526, footnote.

[3] Noyes and Phillips found —59.6° at 18°. *Am. Chem. J.*, **24**, 291.

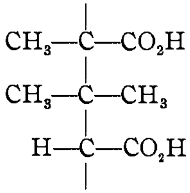


The l-Dihydrohydroxycampholytic Acid, $C_8H_{14}\left\langle\begin{array}{l}CO_2H\\ OH\end{array}\right.$, which remained behind after distillation of the other products with water vapor crystallized from water in granular crystals which melted at 132°. When these crystals were mixed with *d*-dihydrohydroxycampholytic acid, which melts at the same temperature, the melting point rose to about 170°, approaching that of the racemic acid.[1] The rotation in an aqueous solution containing 1.45 per cent. of the acid was $(\alpha)_D = -70.04°$. Noyes and Phillips[2] give +71.5 for the dextro acid.

0.1389 g. required 8.0 cc. of 0.1 *N* NaOH; calculated, 8.07 cc.

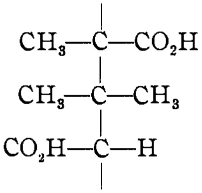
These results establish the identity of the acid as the lėvo form of dihydrohydroxycampholytic acid. The formation of this acid was wholly unexpected. If we represent the configuration of that part of the camphoric acid molecule containing the two asymmetric carbon atoms in the usual manner the results obtained establish the following relations as most probable:

d-Camphoric acid.



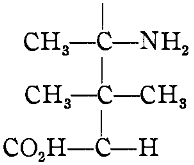
$$\begin{array}{rcl} & | & \\ \mathrm{CH_3}— & \mathrm{C} & —\mathrm{CO_2H} \\ & | & \\ \mathrm{CH_3}— & \mathrm{C} & —\mathrm{CH_3} \\ & | & \\ \mathrm{H}— & \mathrm{C} & —\mathrm{CO_2H} \\ & | & \end{array}$$

l-Isocamphoric acid.



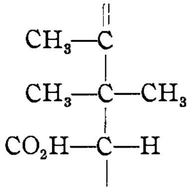
$$\begin{array}{rcl} & | & \\ \mathrm{CH_3}— & \mathrm{C} & —\mathrm{CO_2H} \\ & | & \\ \mathrm{CH_3}— & \mathrm{C} & —\mathrm{CH_3} \\ & | & \\ \mathrm{CO_2H}— & \mathrm{C} & —\mathrm{H} \\ & | & \end{array}$$

Isodihydroaminocampholytic acid.



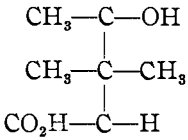
$$\begin{array}{rcl} & | & \\ \mathrm{CH_3}— & \mathrm{C} & —\mathrm{NH_2} \\ & | & \\ \mathrm{CH_3}— & \mathrm{C} & —\mathrm{CH_3} \\ & | & \\ \mathrm{CO_2H}— & \mathrm{C} & —\mathrm{H} \end{array}$$

d-Campholytic acid.



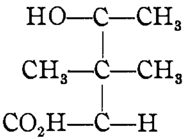
$$\begin{array}{rcl} & \| & \\ \mathrm{CH_3}— & \mathrm{C} & \\ & | & \\ \mathrm{CH_3}— & \mathrm{C} & —\mathrm{CH_3} \\ & | & \\ \mathrm{CO_2H}— & \mathrm{C} & —\mathrm{H} \\ & | & \end{array}$$

Isodihydrohydroxycampholytic acid.



$$\begin{array}{rcl} \mathrm{CH_3}— & \mathrm{C} & —\mathrm{OH} \\ & | & \\ \mathrm{CH_3}— & \mathrm{C} & —\mathrm{CH_3} \\ & | & \\ \mathrm{CO_2H}— & \mathrm{C} & —\mathrm{H} \end{array}$$

l-Dihydrohydroxycampholytic acid.



$$\begin{array}{rcl} \mathrm{HO}— & \mathrm{C} & —\mathrm{CH_3} \\ & | & \\ \mathrm{CH_3}— & \mathrm{C} & —\mathrm{CH_3} \\ & | & \\ \mathrm{CO_2H}— & \mathrm{C} & —\mathrm{H} \end{array}$$

The formation of *d*-campholytic is entirely in accord with the theory, since in this acid one of the asymmetric carbon atoms of the isocamphoric acid has lost its asymmetry through the formation of the double union. The formation of *l*-dihydrohydroxycampholytic acid is not so easily explained. From its method of formation we should expect for this the configuration of an isodihydrohydroxycampholytic acid which is not the optical antipode of *d*-dihydrohydroxycampholytic acid, but which has the methyl and hydroxyl groups reversed. This recalls the fact that *l*-campholytic acid adds hydrobromic acid to form *d*-bromodihydrocam-

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[1] Noyes and Blanchard, *Am. Chem. J.*, 26, 287.

[2] *Am. Chem. J.*, 24, 290.

pholytic acid,[1] taking up the hydrobromic acid asymmetrically. The *d*-campholytic acid would, of course, give *l*-dihydrohydroxycampholytic acid in a similar manner. It is probable from this that the left form of the hydroxy acid is more stable than the expected isodihydrohydroxycampholytic acid and that a portion of the latter is transformed to the former by the action of the nitrous acid—or it may be that *d*-campholytic acid is formed as an intermediate product and that this adds water to form the *l*-dihydrohydroxycampholytic acid.

The study of these compounds will be continued.

URBANA, ILL.

[CONTRIBUTION FROM THE LABORATORY OF SOIL FERTILITY INVESTIGATIONS.]

SOME ACID CONSTITUENTS OF SOIL HUMUS.[2]

BY OSWALD SCHREINER AND EDMUND C. SHOREY.

Received September 27, 1910.

The complex character of the humus or organic matter of the soil need hardly be emphasized here, nor need the complexity of the so-called humic acid be again mentioned other than to remark that so many organic compounds, neutral, basic and acid, have been isolated therefrom in these researches that its claim to chemical unity is absolutely refuted and its non-existence proved. The present paper is a further contribution to the definit knowledge of the chemical nature of this organic soil complex and gives a description of several acids isolated therefrom. The isolation of other acid substances from soils, picolinecarboxylic acid, dihydroxystearic acid and agroceric acid, are reported in earlier papers.[3]

α-Monohydroxystearic Acid, $C_{18}H_{36}O_3$.—When the humus extract of a soil obtained by extraction with dilute alkali is acidified, a brown, flocculent precipitate of the so-called humus substances is formed. If this precipitate is separated by filtration, washed and treated while still moist with boiling 95 per cent. alcohol, a portion of the precipitate goes into solution. The amount of the humus precipitate so dissolved varies with the character of the soil treated, but the alcoholic solution obtained in this way is always dark-colored. On careful evaporation of this alcoholic solution, adding water to keep the volume constant until the alcohol is removed, there is formed a brown or reddish brown precipitate which can be separated by filtration. When so separated, washed and dried, it is in the form of resinous lumps or powder, varying in color, melting point and composition, with the soil from which it was obtained.

On extracting this resinous material with petroleum ether there is obtained an extract generally colorless or light-colored, which on evapora-

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[1] Noyes and Phillips, *Am. Chem. J.*, 24, 24, 291.

[2] Published by permission of the Secretary of Agriculture.

[3] THIS JOURNAL, 30, 1295, 1599 (1908); Bureau of Soils, U. S. Dept. Agr. *Bull.* 53, (1909).