

Chemistry. — *The Reduction of α -Eleostearic Acid. (The Linoleic Acid 10.12 and the Oleic Acid 11.)* By J. BÖESEKEN and J. VAN KRIMPEN.

(Communicated at the meeting of January 28, 1928).

In a paper dealing with the α -eleostearic acid ¹⁾ one of us in conjunction with Mr. J. HOOGLAND has communicated the preliminary results of the catalytic reduction of this acid, in which they came to the conclusion that the conjugated system of three double bonds was attached according to the principle of THIELE, so that first the octadecadeënoic 10—12 acid would be formed, and then the octadecenoic 11-acid.

For, on addition of one mol. of H₂ a compound, was obtained, which, judging from its behaviour towards the solution of WIJS, behaves as a substance with a conjugated system of double bonds, which on further reduction gave a *profuse yield* of the just-mentioned octadecenoic-11-acid (ester).

Now, however, the possibility is not excluded that on taking up the first molecule of hydrogen, one of the end-placed double bonds, either 9 or 13, was hydrogenated, so that the first obtained linoleic acid would be the octadecadeënoic 11 . 13 or the octadecadeënoic 9 . 11-acid, and that on further reduction this has given the octadecenoic-11-acid.

In order to get perfect certainty about the course of the reduction, it was, therefore, necessary, to separate the first-obtained acid, and to determine its constitution.

Besides, the octadecenoic -11-acid had not yet been obtained pure; it contained 5 % stearic acid, and the relatively high melting point 53° was possibly owing to this impurity.

Through improvement of the hydrogenation method, we have succeeded in obtaining the first reduction product of the α -eleostearic acid aethylester pure, and separating from this an acid with a conjugated system melting at 28.5°, and fixing the position of the double bonds in this acid by ozonisation at 10 and 12.

From this a good yield of *sebacic acid* and *caproic acid* was obtained, the middle part being converted to a syrup, the constitution of which we have not yet verified.

We point out here that this acid is isomeric with an acid ¹⁾ that was obtained on distillation of ricinus-elaidic acid, and melts at 53°. This latter has been examined by Mr. W. C. SMIT, who, by determination of the refraction of the ester and from its behaviour towards the solution of

¹⁾ Recueil des trav. chim. 46, 619 (1927).

WIJS, has derived that also this acid possesses a conjugated system. On ozonisation of this a good yield of *azelaic acid* and *heptonic acid* was obtained, while here too the middle two C-atoms have so far not yet yielded a definable compound in considerable quantities. The difference between this acid and that which was obtained on reduction of α -eleostearic acid is therefore confined to the position of the conjugated system, which in this latter acid lies one place further from the carbonyl group.

When the wood oil was hydrogenated with a third of the calculated quantity of hydrogen, the product, investigated according to BERTRAM's method ¹⁾ appeared to contain no stearine. This means that this partial reduction takes place very selectively, as on one side the final product has not been reached, on the other side the about 8 % of oleine, which the wood-oil contains, have been left entirely intact.

Besides it appears from this that our initial product was free from stearic acid.

After the fixing of $\frac{2}{3}$ of the calculated quantity of hydrogen, stearine was, indeed, found, which might have been formed because the oleine was now attached, and the 11-acid is now further reduced.

As we stated above, this 11-acid separated already before was, at first, not obtained pure, it still contained 5 % stearic acid. In fact the acid once recrystallized from alcohol had a melting point of 52°—53°. If it was recrystallized from chloroform and if the first high-melting fractions were removed, the mother liquor appeared to contain a lower-melting compound, which, after repeated recrystallisations from the same solvent, melted constantly at 38°.5. We got the impression that this acid was the only component with one double bond, save the ordinary oleic acid present at the beginning.

By means of ozonisation and melting experiments the 11-oleic (elaidic) acid was found to be identical with the acid separated by S. H. BERTRAM from animal fats and called by him *vaccenic acid*. It is undoubtedly very remarkable that this is found in natural fats, and the question suggests itself whether there might be any connection between the reduction product of wood-oleic acid occurring in the vegetable kingdom, and this product of animal metabolism. The experimental details will be communicated elsewhere, but some constants may be given here.

α -Eleostearic acid. Melt. p. 45° (octodecatricenic-acid 9, 11, 13) was esterified and the aethylester was distilled in cathode-vacuum.

Boil. p. 169—170°.5, refraction at 15° of two separately obtained fractions 1.5043 and 1.5086.

HOOGLAND has also found in three fractions at 15° 1.5042, 1.5064, and 1.5080.

For the present it cannot be decided whether these relatively large differences still point to the presence of stereo isomers; the ester is made

¹⁾ Chem. Weekblad 24, 226 (1927).

from α -eleostearic acid by the aid of alcohol and *hydrochloric acid*, so that an isomerisation is not excluded.

Octodecadienic acid-ethylester obtained by $\frac{1}{3}$ hydrogenation of the α -eleostearic acid ester.

Refraction: $n_D^{15^\circ} = 1.4746$. Mol. Refr. = 96.87.

Calculated = 95.28, Exatation = 1,59 } It follows from this that there is
Iodine value = 109, instead of 180. } a conjugated system in this acid.

The free acid melts at $28^\circ.5$; $n_D^{70^\circ} = 1.4639$.

This ester, as well as the wood oil itself was hydrogenated for $\frac{2}{3}$ part, the product obtained was saponified, and the acids were recrystallized, the largest fraction melted at $38^\circ.5$, showed no changes any more, yielded caproic acid and sebacic acid on ozonisation and presented no lowering of the melting-point with the *vaccenic acid* of BERTRAM (see above) $n_D^{70^\circ} = 1.4432$.

Delft, January 1928.
