COMPOUNDS, PROPERTIES AND ANALYSES

All samples for micro-analyses were dried in a high vacuum at temperatures slightly below the melting points of the respective compounds

				Calculated, %				Found, %				Recovered compound	
Compound	M. p., °C.	$[\alpha]_{5461}$[a]	Formula	Mol. wt.	C	H	N	Mol. wt.	C	H	N	M. p., °C.	$[\alpha]_{5461}$
Phytosterolin	275–288	−33.0	$C_{34}H_{56}O_6$	560	72.8	10.2			72.7	10.4			
Tetraacetate	178.5–179	−13.4	$C_{42}H_{64}O_{10}$	728	69.2	8.9		721 735	69.2	9.2		275–280	−33.0
Tetrabenzoate	178–178.5	+21.6	$C_{62}H_{72}O_{10}$	977	76.2	7.5		960 972	75.9	7.6		275–280	−33.0
γ-Spinasterol	159.5–160	0	$C_{28}H_{46}O$	398	84.3	11.6			84.3	11.5			
γ-Acetate	139.5–140	−14.1	$C_{30}H_{48}O_2$	440	81.7	11.0		441 437 439 440	81.65	11.1		159–159.5	0
γ-Benzoate	118.5–119	−10.3	$C_{35}H_{50}O_2$	502	83.6	10.0		517 525	83.6	10.3		158–159	0
γ-*p*-Nitrobenzoate	200	− 8.9	$C_{35}H_{49}O_4N$	547	76.7	9.0	2.6	554 552 547 555	76.7	8.9	2.7	158–159	0
γ-Phenylurethan	144–145	−15.9	$C_{35}H_{51}O_2N$	517	81.1	9.9	2.7		80.9	10.2	2.9	158–159	0
Dihydro-γ-spinasterol	105.5–106	+24.0	$C_{26}H_{48}O$	400	83.9	12.1			83.9	12.1			
Dihydro-γ-acetate	115.5–116	+12.4	$C_{30}H_{50}O_2$	442	81.4	11.4		444 446	81.2	11.6		105.5–106	+24.0

[a] All rotations were taken with chloroform as solvent, except 1, in which pyridine was used.

Nabenhauer.[6] If this reaction may be considered a method of separating plant sterols into saturated and unsaturated groups, it would then appear that dihydrospinasterol still contains one or more double bonds, for we were unable to detect any sterol material in the carbon tetrachloride layer, when the conditions of the above reaction were employed. Perhaps the inactive double bond resembles the inactive double bond of α-ergostenol.[7] This problem is now under investigation.

Summary

1. A new phytosterolin has been described.

2. Hydrolysis of the phytosterolin yields optically inactive γ-spinasterol.

3. γ-Spinasterol probably contains two double bonds and appears to be an isomer of α-spinasterol.

4. A number of esters of γ-spinasterol have been prepared, as well as dihydrospinasterol and its acetate.

KALAMAZOO, MICH.

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[6] R. J. Anderson and F. P. Nabenhauer, THIS JOURNAL, **46**, 1959 (1924).

[7] M. C. Hart and H. Emerson, *ibid.*, **54**, 1070 (1932); I. M. Heilbron and D. G Wilkinson, *J. Chem. Soc.*, 1708 (1932).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Studies of Conjugated Systems. X. The Electrolytic Reduction of Vinylacrylic Acid

BY IRVING E. MUSKAT AND BARBARA HARRIET KNAPP

In a recent paper[1] on the catalytic hydrogenation of compounds containing conjugated systems of double bonds, we presented a classification of the various types of reducing agents based on their effect on ethylenic double bonds. The classification was as follows.

(1) This group includes the soluble reducing agents, such as ferrous chloride, vanadous chloride, chromous chloride, stannous chloride and titanous chloride. These reagents are known to reduce the carbonyl group, C═O, but are without action on ethylene hydrocarbons.

(2) A second group includes the amalgams of the alkali metals and those of aluminum and magnesium. In this group also belong such reducing agents as the alkali metals and their alcoholates, zinc and hydrochloric acid, and similar reducing agents. The reagents of this group do reduce ethylene double bonds, and will usually reduce a conjugated system in the terminal positions.

(3) Catalytic methods may also be used to hydrogenate ethylene double bonds, but in contrast to the action of the reagents of group (2), reduction of conjugated systems by catalytic means does not occur in the 1,4-positions.

No work has been reported on the electrolytic reduction of compounds containing conjugated systems of double bonds of the type C═C—C═C, but it was stated in our previous publication that electrolytic reduction would probably fall in the second group. The present paper deals with the electrolytic reduction of vinylacrylic acid and shows that it properly belongs in the second group.

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[1] Muskat and Knapp, *Ber.*, **64**, 779 (1931).

It has long been known that, under the proper experimental conditions, hydrogen may be added to an ethylenic linkage electrolytically, but no work on the electrolytic reduction of conjugated compounds has been reported in the literature. In order to approximate conditions previously used, vinylacrylic acid was the conjugated compound chosen for study, since much more work has been done with the electrolytic reduction of unsaturated acids than with the reduction of ethylene hydrocarbons.[2]

The apparatus used for the reduction was a modification of that designed by Pomilio,[3] whereby the amount of hydrogen absorbed could be measured.

The reduction was allowed to continue until approximately one mole of hydrogen per mole of vinylacrylic acid was absorbed. It was possible to isolate a 25–30% yield of a pentenic acid, boiling at 86–87° under 10 mm. pressure, from the reduction products. The low yield may be attributed to the polymerization of the vinylacrylic acid during the course of the reduction. The structure of this pentenic acid was determined by ozonization. A good yield (as high as 87%) of acetaldehyde was obtained by hydrolysis of the ozonide. The aldehyde was identified by the formation of its *p*-nitrophenylhydrazone. The lead salt of malonic acid was also obtained from the hydrolysis products of the ozonide by the addition of lead acetate. In one of the experiments a few crystals of a substance which might have been succinic acid were obtained, but could not be identified. No trace whatever of oxalic acid or formaldehyde was found in the hydrolysis products of the ozonide. This proves that the pentenic acid formed from vinylacrylic acid by electrolytic reduction has the structure $CH_3—CH{=}CH—CH_2—COOH$, and consequently that vinylacrylic acid is reduced electrolytically in the 1,4-positions. Reduction by electrolytic methods, then, belongs in the second group.

The effect of hydrogen-ion concentration on the rate of electrolytic reduction of vinylacrylic acid was determined. It was found that no reduction occurred in a solution which was 0.5 molar in hydrogen ion, nor in alkaline solution. Vinylacrylic acid was reduced most rapidly in a solution which was neutral or faintly acid.

Experimental Part

The apparatus used for the electrolytic reduction of vinylacrylic acid was a modification of the one used by Pomilio.[3] The nickel cathode used in this work was made of a cylinder of nickel gauze (70 mesh) 6 cm. long and 3 cm. in diameter. It was freshly coated each time with spongy nickel by electrolysis of a saturated ammoniacal solution of nickel ammonium sulfate, using a high current density (6–8 amperes), and a potential of 12 volts. The electrolysis was allowed to continue until a good coating of spongy nickel was deposited on the gauze. This usually required thirty to sixty minutes. The cathode was not allowed to dry after the deposition of the spongy nickel.

The vinylacrylic acid to be reduced (17–20 g.) was dissolved in 95% ethyl alcohol (400 cc.), and a small amount of an electrolyte, usually a saturated sodium chloride solution, was added. A potential of 12 volts was used in this work, and a current of 1–2 amperes. It required five to eight hours to reduce 17–20 g. of vinylacrylic acid. The reduction was stopped when approximately one mole of hydrogen per mole of vinylacrylic acid was absorbed.

The reduction mixture was separated from vinylacrylic acid polymer and undissolved sodium chloride by filtration. The filtrate was diluted to three times its volume with water and extracted three times with ether. The ethereal solution was dried over sodium sulfate and the ether was removed by means of suction. The residue was distilled under reduced pressure; almost the entire product distilled over at 86–87° under 10 mm. pressure. At 753 mm. pressure the product boiled at 192.5–193° with decomposition.

Three grams of the pentenic acid obtained was dissolved in chloroform and subjected to ozonization at 0°. The ozonized product was decomposed; from the resulting vapors a 66% yield of acetaldehyde (isolated and identified as the *p*-nitrophenylhydrazone) was obtained.

The aqueous solution remaining from the decomposition of the ozonide was treated in accordance with Ingold's[4] directions. It was refluxed for two hours, and then 30% hydrogen peroxide (40 cc.) was added and the mixture allowed to stand overnight. When a solution of calcium acetate was added to a portion of the resulting solution, no precipitate formed, which showed that there was no oxalic acid present. When the solution was evaporated to dryness only a few crystals remained (about 10 mg.). These melted at 180° and a mixture of them with succinic acid (m. p. 187°) melted at 183°. The melting point of the crystals was determined again on the following day, and it was found that the melting point had fallen to 110°. Since there was so little material it was impossible to purify and identify it. In subsequent experiments no residue was obtained by evaporating the aqueous solution, which had been treated as described above, to dryness. These results show that none of the original amount of vinylacrylic acid was reduced in the 3,4-positions, and very little if any in the 1,2-positions.

Another sample of the pentenic acid (2.5 g.) was ozonized and the ozonide decomposed in the usual manner; 3.9 g. of the *p*-nitrophenylhydrazone of acetaldehyde was obtained. This is 87% of the theoretical amount. The

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[2] Brockman, "Electro-Organic Chemistry," John Wiley and Sons, New York, 1926, p. 275.

[3] Pomilio, *Z. Elektrochem.*, **21**, 444 (1915).

[4] Ingold, *J. Chem. Soc.*, 2033 (1929).

aqueous solution remaining from the hydrolysis was not treated with hydrogen peroxide in this case. A saturated solution of lead acetate was added to it until no further precipitate resulted. A part of this lead salt was suspended in water and treated with dilute hydrochloric acid. The mixture was filtered, and the filtrate was extracted several times (10) with small (15-cc.) portions of ether. On removal of the ether a few crystals remained. These melted at 105°, and a mixture of them with malonic acid (m. p. 132°) melted at 120°. This evidence also indicates that vinylacrylic acid is reduced in the 1,4-positions to form Δ^2-pentenic acid, CH_3—CH=CH—CH_2—COOH; 2.23 g. of the lead salt of malonic acid was obtained from 2.5 grams of the pentenic acid, which is 29% of the theoretical amount. The yield was low, probably because malonic acid decomposed when the solution of the hydrolysis products of the ozonide was warmed to ensure complete removal of the aldehydes.

Several attempts were made to reduce vinylacrylic acid electrolytically in a solution which was 0.5 molar in hydrogen ion. These conditions approximate those used by Pomilio[3] for the reduction of unsaturated acids. In the case of vinylacrylic acid, however, no reduction occurred. An attempt was also made to reduce the sodium salt of vinylacrylic acid. To obtain this, the calculated amount of pure sodium hydroxide was added to a solution of vinylacrylic acid in 95% ethyl alcohol. No reduction occurred under these conditions, but when enough hydrochloric acid was added to the solution to make it approximately neutral to litmus, hydrogen was absorbed. By adding acid and alkali alternately and observing whether or not hydrogen was absorbed, it was found that the most rapid reduction occurred when the solution was neutral or faintly acid.

Summary

Vinylacrylic acid was reduced electrolytically. It was shown that hydrogen is first added in the 1,4-positions to give Δ^2-pentenic acid, CH_3—CH=CH—CH_2—COOH. This is in agreement with the reduction of vinylacrylic acid by means of sodium amalgam, but is in contrast with the catalytic hydrogenation of vinylacrylic acid, whereby hydrogen is added in the 3,4-positions.

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[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Action of Triphenylmethyl Chloride on α-Methyl-*l*-fucoside[1]

BY R. C. HOCKETT[2] AND C. S. HUDSON

By the direct action of triphenylmethyl chloride upon various carbohydrates containing both primary and secondary alcohol groups, Helferich and his colleagues[3] have obtained many sugar derivatives whose primary groups alone are etherified, and have thus amply demonstrated that triphenylmethyl chloride may exercise a preferential action toward primary in the presence of secondary hydroxyl groups. Although the pioneers in this field have offered no general rule that such a selection must invariably occur, a tacit assumption seems to have arisen among other workers that the reaction is so completely specific as to be available for analytical determination of the number of primary hydroxyl groups in any complex molecule of uncertain structure.[4]

This procedure seemed justified *a priori* by such observations as those of Valentin,[5] who found that a number of polyhydroxy alcohols of known constitution absorb the predicted number of triphenylmethyl residues, only the primary alcohol groups being reactive.

The present authors[6] recently observed the reaction of triphenylmethyl chloride with a number of methyl pentosides whose content of primary hydroxyl was uncertain as contingent upon the final assignment of ring structures and therefore considered it necessary to obtain further evidence as to whether a reaction may occur in the presence of secondary hydroxyls only.

α-Methyl-*l*-fucoside, a typical sugar derivative which crystallizes well and which contains four secondary groups but no primary ones, was chosen as a test substance.

This compound readily forms a substitution derivative when treated at room temperature with a dry pyridine solution of triphenylmethyl chloride under the conditions described by Helferich.[3a] The product has been isolated both as a crystalline mono-ethyl alcoholate and as an anhydrous powder. Its analyses indicate that it is a monotrityl-α-methyl-*l*-fucoside. The prop-

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[1] This paper was delivered before the Organic Division of the American Chemical Society at Washington, D. C., in March, 1933. Publication is authorized by the Surgeon General, U. S. Public Health Service.

[2] National Research Fellow during a part of this work.

[3] (a) *Ann.*, **440**, 1 (1924); (b) **447**, 19, 27 (1926); (c) *Ber.*, **58**, 872 (1925).

[4] (a) Josephson, *Ann.*, **472**, 230 (1929); *Ber.*, **62**, 313 (1929); (b) Pacsu, THIS JOURNAL, **53**, 3099 (1931).

[5] F. Valentin, *Coll. Czechoslov. Chem. Comm.*, **3**, 499 (1931).

[6] Hockett and Hudson, THIS JOURNAL, **53**, 4456 (1931).