[Contribution No. 724 from the Department of Chemistry, University of Pittsburgh]

X-Ray Diffraction Analysis of Vaccenic Acid[1]

By James H. Benedict and B. F. Daubert

In a previous communication[2] from this Laboratory the *trans* configuration of natural vaccenic acid was confirmed by comparison of its infrared absorption data with those of oleic and elaidic acids. Subsequent to this work a comparison of the infrared data was made of a synthetic vaccenic acid submitted to us by Dr. F. M. Strong,[3] with the natural acid. On the basis of the comparative infrared results and mixed melting points it was concluded by Strong[3] that the synthetic vaccenic acid was of *trans* configuration and accordingly identical with the natural acid.

In order to provide further identification data, the natural and synthetic vaccenic acids were submitted to X-ray diffraction analysis, and the data compared with those for elaidic acid. Also, since the earlier X-ray diffraction data for elaidic acid[4] were very meager a more detailed analysis was made and is herewith reported.

The comparative X-ray data in Table I indicate that synthetic vaccenic and elaidic acids possess similar crystal structures since the two patterns have nearly identical long and short spacings. The dissimilarities in the diffraction pattern of natural vaccenic acid as compared to the patterns for synthetic vaccenic and elaidic acids may be attributed to differences in the angles of tilt in the crystals, and possibly to differences in the structure of the acids.

The exceedingly shorter long spacing for natural vaccenic acid as compared to elaidic acid could readily be explained by a greater angle of tilt in the natural vaccenic crystal structure since both acids are of *trans* configuration and differ only in the position of the double bond. It should also be noted that a vaccenic acid obtained as a product of the hydrogenation[5] of β-elaeostearic acid gave a pattern essentially identical to that obtained on the natural vaccenic acid.

Experimental

The elaidic acid was prepared by isomerization of highly purified oleic acid with nitrous acid according to the method of Lyutenberg.[6] It was recrystallized several times from ethyl ether and methyl alcohol; m. p. 44.5°, I. V. 89.9 (calcd. 89.9).

The vaccenic acid used in this study was a portion of the same acid, isolated from beef tallow, which was used in the infrared studies previously described.[2] The synthetic vaccenic acid was kindly furnished us by Dr. F. M. Strong of the University of Wisconsin and was prepared by methods described by Strong and co-workers.[3]

X-Ray Diffraction Analysis.—The X-ray diffraction patterns were obtained in a manner analogous to that previously described.[7] The solvent-crystallized acids were analyzed and the data are given in Table I.

Table I

X-Ray Diffraction Data, in Å.

(*hkl*)	Elaidic acid	Vaccenic acid synthetic	Vaccenic acid natural
		Long Spacings	
001	48.9 VS	48.9 VS	39.8 VS
002	24.3 VW	24.4 W+	19.8 W
003	16.3 M	16.3 M	13.4 M+
004			
005	9.81 M	9.78 M	8.02 M
006			
007	6.97 W	7.00 W+	5.70 VW
008		6.12 VW	
009		5.42 VW	
0010	4.89 VW	4.88 VW	
Av. d	48.9	48.9	39.9
M. p.	44.5°	44.0°	42.5°
		Short Spacings	
	4.57 M−	4.56 M	4.64 M
	4.12 VS	4.12 VS	4.36 W+
	4.00 M	4.01 W+	4.16 VS
	3.74 S	3.71 S	4.02 W
	3.65 S	3.66 S	3.84 S
	3.47 W	3.47 M−	3.62 M−
	3.38 W	3.25 W	3.43 VW
	3.27 W	2.94 M+	3.35 M
	2.92 M+	2.68 W	3.03 M−
	2.75 W	2.62 W	2.89 W
	2.70 W	2.48 S−	2.78 W
	2.58 VW	2.34 M−	2.67 VW
	2.49 M+	2.26 M	2.46 M
	2.31 M−	2.23 S−	2.39 M−
	2.23 S−	2.18 M−	2.32 W
	2.20 M	2.13 W+	2.24 M
	2.15 W	1.92 W	2.19 M
	2.06 M−		2.06 W
	1.94 VW		1.88 VW
	1.86 VW		1.85 VW
	1.85 W		1.73 W
	1.77 VW		
	1.74 VW		

To determine the presence or absence of other polymorphic forms, the acids packed in nylon tubes were fused, cooled rapidly, and then stabilized by holding at −20° for four days. After X-ray exposure, melting points were determined. The fused samples under the experimental conditions indicated gave diffraction patterns similar to those obtained for the solvent-crystallized acids.

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(1) A Research Fellowship grant of the Procter and Gamble Company in support of this investigation is gratefully acknowledged.

(2) Rao and Daubert, This Journal, **70**, 1102 (1948).

(3) Ahmad, Bumpus and Strong, *ibid.*, **70**, 3391 (1948).

(4) Muller, *J. Chem. Soc.*, **123**, 2043 (1923); Muller and Shearer, *ibid.*, **123**, 3156 (1923).

(5) Woltemate and Daubert, unpublished results.

(6) Lyutenberg, *Fettchem. Umschau.*, **42**, 89 (1935).

(7) Daubert and Sidhu, This Journal, **70**, 1884 (1948); **68**, 2603 (1946).

Summary

X-Ray data are reported for natural vaccenic acid, synthetic vaccenic acid and elaidic acid.

PITTSBURGH, PA. RECEIVED MAY 7, 1949

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STATE UNIVERSITY OF IOWA, IOWA CITY, IOWA]

On the Existence of the Higher Oxides of Neodymium[1]

BY ALEXANDER I. POPOV AND GEO. GLOCKLER

A literature survey showed that the question of the existence of the higher oxides of neodymium still remains unsettled. Earlier workers with the rare earth elements often claimed to have obtained NdO_2 and Nd_2O_5 either by heating the sesquioxide in air[2] or by heating the oxalate in oxygen.[3,4] Mark[5] claimed to have obtained excess of combined oxygen in a didymium–cerium mixture, which he attributed to the formation of neodymium "superoxide." Waegner[3] and Popovici[6] both claimed to have obtained Nd_2O_5 by fusion of the oxalate or the trifluoride with ammonium nitrate.

On the other hand Marsh[7] in 1946 repeated the work of Mark and failed to obtain any evidence for the formation of the higher oxides of neodymium. He also postulated that Waegner's and Brauner's results were due to the unusual stability of the basic neodymium oxide NdO(OH). This compound was first prepared by Joye and Garnier[8] in 1912 and seems to have the same reflection spectrum as Waegner's "superoxide." Pagel and Brinton[9] in 1929 attempted to oxidize the sesquioxide of neodymium by heating it to 350° with oxygen under 215-lb. pressure but found no evidence of oxidation.

Experimental Results

In an attempt to clarify this question the work of the earlier investigators was repeated. It was found that heating the sesquioxide in a current of oxygen at temperatures varying between 500 and 1000° did not result in any oxidation of the compound.

It was next decided to try the combustion of neodymium oxalate in a current of oxygen. The oxalate was obtained by precipitation of an acidified neodymium nitrate solution with oxalic acid and drying the precipitate at 120°. Weighed portions of the oxalate, in a porcelain boat, were introduced into an electrical combustion furnace. Dried commercial oxygen was passed while the furnace was progressively brought to the desired temperature. The period of heating was varied from one to two and a half hours. The resulting oxide was cooled in a current of dry nitrogen, weighed and dissolved in an acid potassium iodide solution. Liberated iodine was titrated with a standard sodium thiosulfate solution and the percentage of "active" oxygen calculated.

Seven experiments were made at 550, 700 and 950°. The average amount of "active" oxygen found in the product was 0.1%. No significant variation of this figure with temperature was observed. The active oxygen percentage in NdO_2 should be 4.54. The small amount of "active" oxygen found is probably due to traces of praseodymium, because the present sample of neodymium oxide was faintly grayish in color in comparison with a small sample of very pure neodymium oxide which originated in Professor Rolla's laboratory in Florence and which was at our disposal.

Neodymium oxalate which was heated to 550° was reintroduced into the combustion tube after being weighed and was heated again to 1000°. A tared drying tube was attached to the system and again a current of dry oxygen was passed. After heating the sample for one hour the boat was withdrawn and the weight of the drying tube redetermined. A blank was also run and gave negative results within the limits of experimental error (Table I).

TABLE I

DEHYDRATION OF BASIC NEODYMIUM OXIDE

	Sample, g.	Water obtained, mg.	Water calcd., mg.
Expt. 1	0.2412	13.0	12.2
Expt. 2	.2099	10.7	10.6
Expt. 3	.3714	19.0	18.9

It thus seems that the supposition of Marsh is correct and that by heating hydrated neodymium oxalate to 550° the basic oxide of the element is formed, which subsequently decomposes in the neighborhood of 1000° to the sesquioxide and water.

The fusion of neodymium oxalate, sesquioxide or the trifluoride with ammonium nitrate also failed to give any higher oxides.

As the fusion of praseodymium oxide with sodium chlorate yields praseodymium dioxide,[10]

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[1] From a thesis presented by Alexander I. Popov to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] F. R. M. Hitchcock, THIS JOURNAL, **17**, 483 (1895).

[3] A. Waegner, *Z. anorg. allgem. Chem.*, **42**, 118 (1904).

[4] B. Brauner, *Coll. Czechoslov. Chem. Commun.*, **5**, 279 (1932).

[5] R. Mark, *Ber.*, **35**, 2370 (1902).

[6] J. Popovici, *ibid.*, **41**, 634 (1908).

[7] J. K. Marsh, *J. Chem. Soc.*, 20 (1946).

[8] P. Joye and C. Garnier, *Compt. rend.*, **154**, 510 (1912).

[9] H. A. Pagel and Paul H. Brinton, THIS JOURNAL, **51**, 42 (1929).

[10] W. Prandtl and K. Huttner, *Z. anorg. allgem. Chem.*, **149**, 235 (1925).