294. *The Oxidation of Monoethenoid Fatty Acids and Esters. The Preparation and Catalytic Oxidation of Highly Purified Brassidic Acid by Gaseous Oxygen.*

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Modified processes are detailed for the preparation of highly purified brassidic acid, from the fatty acids of rape oil, by making use of urea complexes.

A study of the changes occurring during, and of the oxidation products of, the catalytic oxidation of brassidic acid by gaseous oxygen at 120° and 73° with uranyl brassidate as catalyst has shown that there is little rupture of the carbon chain, the main products being dihydroxybehenic acid and an oily monomeric complex containing keto-hydroxy- or keto-unsaturated derivatives. Brassidic acid hydroperoxide is more stable than that of erucic acid, at moderate temperature, and the *trans*-acid is again generally less susceptible to oxidation than the *cis*-isomer. The results of high-temperature oxidation have confirmed existing views on the mechanism of oxidation of monoethenoid fatty acids.

The object of the present investigation was to compare the course of catalytic autoxidation of brassidic acid (*trans*-docos-13-enoic acid) with that of the *cis*-isomer (Skellon and P. E. Taylor, *J.*, 1952, 1813; Dorée and Pepper, *J.*, 1942, 477), and elaidic acid (*trans*-octadec-9-enoic acid) (Skellon and Thruston, *J.*, 1949, 1626, 1953, 138). Brassidic acid was obtained by isomerisation of purified erucic acid, prepared by adaptation of Schlenk and Holman's procedure (*J. Amer. Chem. Soc.*, 1950, **72**, 5001) for the separation of urea complexes of the fatty acids. This method is superior to the lead–lithium salt process, the product being entirely free from polyethenoid fatty acids containing the penta-1 : 4-diene system.

Dorée and Pepper (*loc. cit.*) oxidised brassidic and erucic acid by using hydrogen peroxide in the presence of osmium tetroxide, also potassium permanganate in neutral and alkaline solutions; the dihydroxy- and peroxy-acids recovered corresponded to those obtained by Hilditch and other workers, from oleic and elaidic acid. By oxidising erucic acid with oxygen at 70° and 120° in the presence of a cobalt catalyst, Dorée and Pepper obtained peroxybrassidic acid (m. p. 70°), but no scission products or keto-derivatives.

In the present work brassidic acid has been oxidised at 73° and 120° with oxygen by using 0·05% uranium (as uranyl brassidate) as catalyst. At 73° the peroxide content steadily increased with time, to 0·465% of active oxygen at 36 hr., with fall in iodine and acid value. Decomposition of peroxide did not occur, and analysis confirmed the comparative stability of the hydroperoxide at this temperature.

In contrast, at 120°, a maximum peroxide content (0·29% of active oxygen, corresponding to 6·7% of brassidic hydroperoxide) was reached in 1 hr., after which the peroxide rapidly decomposed; the iodine value fell to 50% of the original value in 5 hr., and the acid value steadily decreased.

After 10 hr. at 120°, there was little evidence either of degradation of the carbon chain or of dimerisation. No monoperoxy-acids were isolated (cf. erucic acid; Dorée and Pepper, *loc. cit.*), but after saponification, dihydroxybehenic acid (8%) and a monomeric oil (72%), containing keto-hydroxy- or keto-unsaturated compounds (25%) were recovered. This oxidation of brassidic acid follows a similar course, in general, to that described for elaidic acid (Skellon and Thruston, *loc. cit.*), the initial hydroperoxide undergoing transition or decomposition mainly to a complex ketonic oil.

The formation of these ketonic complexes after decomposition of the peroxide and before polymerisation is apparently a characteristic feature in autoxidation of unsaturated fatty acids and esters.

Experimental

Preparation of Erucic Acid by Urea-complex Formation.—The mixed fatty acids (140 g.; I.V., 76; acid val., 182) from rape oil were dissolved in methanol (2500 ml.), and urea (400 g.)

added to the hot solution. On cooling, the urea complex (270 g.) separated as needles. This was warmed with dilute hydrochloric acid (1000 ml.), and the liberated fatty acids (Fraction 1; 94 g.; I.V., 76·1; acid val., 171) washed with hot water and extracted with light petroleum. Methanol (1500 ml.) was distilled from the mother-liquor; the residue, on cooling, deposited a further 110 g. of urea complexes, from which 24 g. of acids (I.V., 102; acid val., 180) were obtained. These consisted mainly of oleic and polyethenoid acids.

Lead acetate (5 g.) in boiling alcohol was added to the free acids (fraction 1; 94 g.) in ethyl alcohol and the mixture refluxed for a few moments and then set aside. The precipitated lead salts (12 g.) were converted into the fatty acids (6 g.; I.V., 30). The filtrate was again treated with lead acetate, giving insoluble lead salts, from which erucic acid (51 g., 36%) was obtained. After recrystallisation from alcohol the erucic acid had I.V., 74, acid val., 165·3.

Preparation of Erucic Acid via *the Lead Salt.*—To a boiling alcoholic solution of the mixed fatty acids (200 g.) from rape oil, lead acetate (88 g. in 100 ml. of boiling alcohol) and a few drops of acetic acid were added, and the mixture was refluxed for 2 mins. and then set aside. The lead salts were filtered off and acidified, saturated fatty acids (I.V., 21·7) separating. The filtrate was again treated with lead acetate (25 g. in 300 ml. of boiling alcohol), and the lead salts acidified, yielding erucic acid (I.V., 74), after several crystallisations of the product (40 g.) from alcohol at 0°. A further 25 g. of erucic acid were similarly obtained from the filtrate. After repeated recrystallisation from alcohol, the erucic acid had I.V., 74·5; acid val., 165·2; m. p. 33·5° (Calc. for $C_{22}H_{42}O_2$: I.V., 75·0; acid val., 165·8).

Isomerisation of Erucic Acid to Brassidic Acid.—Erucic acid was isomerised in batches to brassidic acid by use of nitrogen oxides (cf. Dorée and Pepper, *loc. cit.*). The product (yield, 65—70%) had m. p. 60° (I.V., 75°; equiv., 338).

Catalytic Autoxidation of Brassidic Acid.—The apparatus consisted of a large Pyrex tube (6 in. × 2·5 in.) fitted with an oxygen-inlet tube, thermometer, and stirrer and was fitted into a thermostatically controlled oven. Since the reaction is exothermic, the oven-temperature during oxidations was somewhat lower than that registered in the apparatus. Uranium brassidate (equivalent to 0·05% of uranium) was dissolved in the acid, and dry oxygen was bubbled through, samples of the mixture being withdrawn hourly. Carbon dioxide formation was estimated by passing the evolved gases through baryta water.

Catalytic autoxidation of brassidic acid.

At 73°.

Time, hr.	1	2	3	4	5	6	7	12	18	24	36
Active O, %	0·03	0·033	0·027	0·033	0·040	0·037	0·056	0·111	0·185	0·234	0·465
I.V.	76·5	77·4	73·0	77·8	68·1	69·2	66·7	67·4	—	68·5	58·0

At 120°.

Time, hr.	1	2	3	4	5	10
Active O, %	0·292	0·245	0·210	0·154	0·109	0·010
I.V.	64·1	59·5	51·8	47·5	41·0	36·5
Acid val.	164·8	163	163·7	162·3	158·3	—

The product of oxidation for 10 *hr. at* 120°. Only 0·02 equiv. of carbon dioxide was evolved from 1 equiv. of brassidic acid, indicating little chain-degradation. The product [Found: *M* (ebullioscopic), 335; I.V., 36·5; active oxygen, 0·010%] of 10 hr. oxidation slightly reduced Fehling's solution. A portion (13 g.) was warmed with alcoholic potassium hydroxide (10 g. in 50 ml. of alcohol), and the alcohol then distilled off. After acidification and cooling, the brown product was repeatedly extracted with cold light petroleum (b. p. 40—60°). Removal of solvent and recrystallisation of the residue (2·6 g.) from alcohol gave unchanged brassidic acid (0·8 g.), m. p. 60°, acid val., 167·3. On removal of alcohol from the filtrate, a light brown oil (acid val., 155; I.V., 42·3) remained, which did not reduce Fehling's solution. The fraction, insoluble in cold light petroleum, was extracted with ether giving, on removal of solvent, a dark-brown, waxy solid (4·1 g.) from which unchanged brassidic acid and a residual oil (acid val., 174·4; I.V., 34·4) were recovered. Recrystallisation of the residue from the ether extraction gave dihydroxybehenic acid, m. p. and mixed m. p. 132° (Found: acid val., 148. Calc. for $C_{22}H_{44}O_4$: acid val., 150).

The product from a similar oxidation was examined portionwise for hydroxyketo-derivatives and peroxybrassidic acid. As a modification of King's method (*J.*, 1936, 1788) for the isolation of hydroxyketostearic acids, a solution of the product (5 g.) in chloroform (50 ml.) was kept below 0° for 24 hr.; no solid separated. The chloroform was therefore removed, the residue taken up in light petroleum (b. p. 40—60°; 200 ml.), and, after 24 hr. at −10°, the residue was separated and again treated with chloroform and light petroleum. The product (I.V., 19; acid val., 126) readily reduced Fehling's solution, indicating a hydroxy-ketone (acyloin) or an unsaturated ketonic derivative. The remainder of the oxidation product (10 g.) was examined for peroxybrassidic acid, by dissolution in alcohol and cooling at 0° for 48 hr. The product (1·9 g.), m. p. 60° (I.V., 66·1; acid val., 148·6; mean equiv., 376), was not identifiable with peroxybrassidic acid (Calc. for $C_{22}H_{44}O_3$: equiv., 356) and probably consisted of unchanged brassidic acid, mixed with the ketol derivative (Calc. $C_{22}H_{42}O_4$: equiv., 370).

The oil obtained on evaporation of the alcoholic filtrate had I.V., 37, acid val., 140, and reduced Fehling's solution (Found : CO, 1·9%). Extraction with cold light petroleum (b. p. 40—60°) gave a pale oil [I.V., 39·4; acid val., 99; *M* (ebullioscopic), 232] whilst the insoluble residue (I.V., 23·1; acid val., 125) also strongly reduced Fehling's solution.

The oily oxidation complexes of brassidic acid (and similar products of other oxidised monoethenoid fatty acids), unlike pure ketols formed by oxidation with neutral permanganate, do not form crystalline dinitrophenylhydrazones or semicarbazones.

Modified special methods of determining CO in oxidised fatty acids, esters, and parent fats are under investigation.

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