that some or all of the water that was formed was retained by the surface. Desorption of appreciable amounts of water then would not occur until the surface had become fully covered with adsorbed water, the attainment of that saturated state being helped by the decline of the surface by the reduction process.

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1. G. Gallo and M. Del Guerra. Ann. Chim. Rome, **41**, 51 (1951).
2. V. A. Romanov, V. M. Drozdova, and G. A. Shif. Uch. Zap. Leningr. Gos. Univ. Ser. Khim. Nauk, No. 10, 79 (1951).
3. P. Faeth. Adsorption and Vacuum Technique. Rept. No. 66100-2-X, Univ. Michigan. 1962.
4. S. Brunauer, P. H. Emmett, and E. Teller. J. Am. Chem. Soc. **60**, 309 (1938).

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SUBSTITUTED HYDANTOINS AND OROTIC ACIDS

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The structure of 5-(carbethoxymethylidene)-hydantoin (1) was established by Mitchell and Nyc (2, 3), who showed that treatment of the compound with aqueous base produced first the salt of 5-(carboxymethylidene)-hydantoin which was subsequently isomerized to the salt of orotic acid. That the rearrangement occurred before acidification was demonstrated by following the change in the ultraviolet spectrum of the basic solution (3). Direct evidence that the ring of the orotic acid was in fact established in the alkaline medium was obtained in the present investigation through the observation that potassium orotate precipitated directly from the reaction mixture.

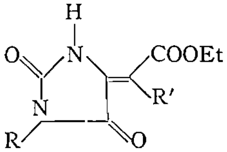
Clerk-Bory and Mentzer (4) extended the method to the preparation of mono- and di-substituted orotic acids. The hydantoin acid could not be isolated as an intermediate when there was present a substituent at the 3-position of the starting material. We also failed to isolate the hydantoin-acid intermediate expected on the treatment of 3-methyl-5-(carbethoxybenzylidene)-hydantoin with base. The acid, was however, obtained by acid-catalyzed hydrolysis of the ethyl ester.

The main purpose of this communication is to report the hydantoin derivatives listed in Tables I and II and the substituted orotic acids shown in Table III. The methods used were virtually the same as those previously reported (2–4). Except for 3-phenyl-5-(carboxymethylidene)-hydantoin, as previously shown (4), the ultraviolet absorption maxima using 95% aqueous ethanolic solutions for the hydantoin derivatives, 296–309 mμ ($\epsilon_{\max} = 10\,000 - 14\,500$), were to higher wavelength than those for the substituted orotic acids, 280–283 mμ ($\epsilon_{\max} = 7\,000 - 9\,500$). For the 3-phenyl compound, the maximum absorption was at 280 mμ ($\epsilon_{\max} = 14\,500$).

The infrared absorption frequencies observed in the carbonyl region are reported in Tables I–III. As seen, the hydantoin derivatives, as Nujol mulls, showed characteristic absorption in the region 1 758 – 1 803 cm^{-1}. The multiple strong absorptions in the carbonyl region displayed by substituted orotic acids are also present in the spectrum of

TABLE I

Substituted hydantoin esters

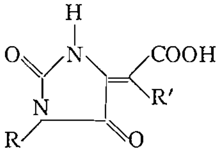


Compound				Elemental analysis					Infrared absorption,* cm^{-1} (Nujol mull)			
R	R′	Formula		% C	% H	% N	Melting point, °C	Yield, %				
CH_3	H	$C_8H_{10}N_2O_4$	Calcd.	48.48	5.09	14.14	141	75	1 795 (m)	1 740 (s)	1 695 (w)	1 665 (s)
			Found	48.34	4.95	14.64						
C_6H_5	H	$C_{13}H_{12}N_2O_4$	Calcd.	60.00	4.65	10.76	191	63	1 772 (m)	1 723 (s)	1 706 (w) 1 689 (s)	1 665 (s)
			Found	60.44	4.60	10.68						
H	C_6H_5	$C_{13}H_{12}N_2O_4$	Calcd.	60.00	4.65	10.76	183–184	15	1 780 (s)	1 735 (s)	1 666 (s)	
			Found	59.79	4.84	10.74						
CH_3	CH_3	$C_9H_{12}N_2O_4$	Calcd.	50.93	5.70	13.20	108–109	62	1 770 (s)	1 715 (s)	1 682 (s)	1 640 (s)
			Found	51.22	5.75	12.99						
CH_3	n-C_4H_9	$C_{12}H_{18}N_2O_4$	Calcd.	56.68	7.13	11.02	118–119	28	1 775 (s)	1 718 (s)	1 680 (s)	1 636 (s)
			Found	56.55	7.30	10.96						
CH_3	C_6H_5	$C_{14}H_{14}N_2O_4$	Calcd.	61.31	5.15	10.21	138–139	29	1 773 (s)	1 720 (s)	1 678 (s)	1 620 (m)
			Found	61.55	5.23	10.34						

*Letters in parentheses indicate the intensity of absorption; vs = very strong; s = strong; m = medium; w = weak.

TABLE II

Substituted hydantoin acids



Compound			Elemental analysis				Melting point, °C	Yield, %	Infrared absorption,* cm^{-1} (Nujol mull)			
R	R′	Formula		% C	% H	% N						
H	n-C_4H_9	$C_9H_{12}N_2O_4$	Calcd.	50.93	5.70	13.20	231–233	—	1 803 (s)	1 720 (s)	1 688 (m)	1 635 (w)
			Found	51.51	5.82	13.11	(decomp.)					
H	C_6H_5	$C_{11}H_8N_2O_4$	Calcd.	56.90	3.47	12.07						
			Found†	56.92	3.69	12.21	220–240	86	1 757 (m)	1 710 (s)	1 675 (s)	1 630 (m)
			Found‡	57.00	3.44	11.91	220–240		1 785 (w)	1 718 (s)	1 680 (s)	1 628 (m)
									1 760 (s)			
CH_3	C_6H_5	$C_{12}H_{10}N_2O_4$	Calcd.	58.54	4.09	11.38	227–240	21	1 773 (s)	1 730 (s)	1 674 (s)	1 620 (m)
			Found	58.34	4.20	11.47						

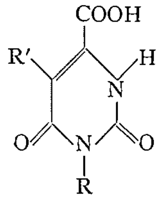
*See footnote * in Table I.

†Colorless crystals from ethanol-benzene.

‡Yellowish crystals from water; see Hahn and Endicott (7) for similar phenomena.

TABLE III

Substituted orotic acids



Compound		Formula	Elemental analysis				Melting point, °C	Yield, %	Infrared absorption,* cm^{-1} (Nujol mull)			
R	R′			% C	% H	% N						
H	n-C_4H_9†	$C_9H_{12}N_2O_4$	Calcd.	50.93	5.70	13.20	314	68	1 740 (s)	1 690 (m)	1 612 (m)	1 583 (w)
			Found	51.51	5.87	13.26	(decomp.)					
H	C_6H_5	$C_{11}H_8N_2O_4$	Calcd.	56.90	3.47	12.07	330–340	—	1 736 (s)	1 692 (s)	1 620 (s)	1 592 (m)
			Found	57.01	3.55	12.19	(decomp.)					
C_6H_5	H‡	$C_{11}H_8N_2O_4\cdot H_2O$	Calcd.	52.80	4.03		278–280	98	1 725 (w)	1 705 (s)	1 655 (vs)	1 640 (vs)
			Found	52.97	4.05							
CH_3	H§	$C_6H_6N_2O_4$					325	90	1 734 (s)	1 709 (s)	1 635 (vs)	1 593 (vs)
							(decomp.)					
CH_3	CH_3	$C_7H_8N_2O_4$	Calcd.	45.66	4.38		286–289	88	1 709 (s)	1 681 (s)	1 640 (vs)	
			Found	45.92	4.63		(decomp.)					
CH_3	n-C_4H_9	$C_{10}H_{14}N_2O_4$	Calcd.	53.10	6.20	12.39	240–242	85	1 706 (s)	1 679 (m)	1 643 (vs)	1 610 (vs)
			Found	53.05	6.36	12.48						
CH_3	C_6H_5	$C_{12}H_{10}N_2O_4$	Calcd.	58.54	4.09		267–270	37	1 724 (s)	1 682 (m)	1 635 (vs)	
			Found	58.52	4.17							

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*See footnote * in Table I.

†Previously reported (4), m.p. 281 °C.

‡Previously prepared by different route (8), m.p. 280 °C.

§Previously prepared by direct methylation of orotic acid (9), m.p. 306–311° (decomp.). The n.m.r. spectrum of the sodium salt in deuterium oxide showed, as expected, signals at 6.72 τ (3 protons) and 3.81 τ (1 proton).

orotic acid [1 695 (s), 1 645 (s), and 1 605 (w) cm^{-1}] and seem to require that these compounds exist in the keto forms rather than in the pyrimidine form sometimes inferred (5, 6) for orotic acid. The proton magnetic resonance spectra of the compounds and the neutral equivalents of the acids were in agreement with those expected for the structures indicated. Several of the compounds listed, especially the orotic acids, showed crystalline transitions in the course of the melting-point determinations.

EXPERIMENTAL

Substituted Hydantoins Esters (Table I)

Diethyl ketosuccinate or the appropriately 3-substituted diethyl ketosuccinate was condensed with either urea or the monosubstituted area following the directions reported by Clerk-Bory and Mentzer (4). When the product did not crystallize directly from the reaction mixture, it was isolated by solvent removal *in vacuo* for crystallization.

Substituted Hydantoin Acids (Table II)

Mild alkaline hydrolysis followed by acidification and recrystallization of the precipitate from aqueous ethanol (4) provided the desired acid except for 3-methyl-5-(carboxybenzylidene)-hydantoin. This compound was obtained by refluxing a solution of the ester (12 g) in 400 ml of a 1:1 mixture of ethanol and 1% aqueous perchloric acid for 9 days. The acid was isolated from the incompletely hydrolyzed product in the usual manner and purified by recrystallization from ethanol–benzene.

Substituted Orotic Acids (Table III)

Except as described below, the ethyl esters reported in Table I were heated for about 4 h in refluxing 2 *N* aqueous potassium hydroxide (4). In order to achieve homogeneous conditions, ethanol was added at the beginning of the heating period until solution was complete. The ethanol was then removed during the course of the reaction. In each case, when the reaction was stopped, the ultraviolet absorption spectrum of the solution no longer showed the maximum absorption above 290 mμ originally present for the hydantoin derivative. In the preparation of the 3-methyl- and 3-phenyl-orotic acids, the reaction mixture was stirred at 50° and the ethanol was not removed.

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1. R. Müller. J. Prakt. Chem. **56**, 475 (1897).
2. H. K. Mitchell and J. F. Nyc. J. Am. Chem. Soc. **69**, 674 (1947).
3. J. F. Nyc and H. M. Mitchell. J. Am. Chem. Soc. **69**, 1383 (1947).
4. C. Clerk-Bory and C. Mentzer. Bull. Soc. Chim. France, 436 (1958).
5. H. Gershon. J. Org. Chem. **27**, 3507 (1962).
6. G. D. Daves, F. Baiocchi, R. K. Robins, and C. C. Chang. J. Org. Chem. **26**, 2755 (1961).
7. D. A. Hahn and M. M. Endicott. J. Am. Chem. Soc. **59**, 2741 (1937).
8. M. R. Atkinson, M. H. Maguire, R. K. Ralph, G. Shaw, and R. N. Warrener. J. Chem. Soc. 2363 (1957).
9. J. J. Fox, N. Yung, and I. Wempen. Biochim. Biophys. Acta, **23**, 295 (1957).

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RADIATION CHEMISTRY OF POTASSIUM PEROXYDISULFATE

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This note gives the results obtained in a study of the radiation chemistry of potassium peroxydisulfate. Samples of the solid compound were irradiated with ^{60}Co γ-rays after which they were dissolved in water and the resulting solutions analyzed.