3. The diacetate in acetic acid solution at room temperature gives a mixture of the tetrabromo derivative and a dibromo-acetoxynaphthol.
4. The dibromo compound is oxidized by chromic acid to a naphthoquinone; so also is the tribromo derivative, but the tetrabromo compound oxidizes with the loss of one bromine atom to the same quinone.
5. The naphthoquinones are easily reduced to dihydric and trihydric naphthols.
6. The hydroxynaphthoquinones have the 1,4-quinoid structure, as proved by the pyroboro-acetate reagent.
7. A variety of derivatives is described.
8. The naphthoquinones are isomeric with certain halogenated juglones but are not identical with any.

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LEVULINIC ACID AND ITS ESTERS

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While levulinic acid[1] is formed quite easily from glucose and other carbohydrates by the action of boiling dilute mineral acids, the mechanism of the reaction is still obscure and there is practically no good convenient method for the preparation of a large amount of the acid in the laboratory. The common procedure described by Rischbieth[2] offers experimental difficulties and gives only low yields due to incomplete disintegration of the carbohydrate (starch). McKenzie[3] has recently described a procedure in which cane sugar is hydrolyzed with dilute hydrochloric acid, the solution is evaporated to dryness and the residue extracted with ether. We have not found that the new method has any advantage over those previously described.

By repeated trials we have found commercial glucose to be a better starting material than sucrose. The yields were higher and the amount of humus substance precipitated was comparatively less. Another experimental observation we have made is that the action proceeds rapidly if the temperature of the solution is raised to 110°. At temperatures below this,

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[1] (a) Nöldecke, *Ann.*, **149**, 224 (1869); (b) v. Grote and Tollens, *ibid.*, **175**, 181 (1875); (c) v. Grote, Kehrer and Tollens, *ibid.*, **206**, 207, 226, 233, 257 (1881); (d) Tollens, *Ber.*, **14**, 1950 (1881); (e) Kent and Tollens, *Ann.*, **227**, 227 (1884); (f) Block, Kreckeler and Tollens, *ibid.*, **238**, 287 (1887); (g) Wehmer and Tollens, *ibid.*, **243**, 314 (1888); (h) Schuette and Sah, THIS JOURNAL, **48**, 3164 (1926).

[2] Rischbieth, *Ber.*, **20**, 1773 (1887).

[3] McKenzie, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1929**, Vol. IX, p. 50.

the transformation of hexose to levulinic acid is very slow and incomplete and a large amount of intermediate decomposition product, oxymethylfurfural, accumulates and is lost owing to volatilization on subsequent distillation or evaporation.

Although there are quite a few functional derivatives of levulinic acid described in the literature, the number is still rather small. Of the esters,[4] only three, methyl, ethyl and *n*-propyl, have been synthesized. The ethyl ester has been quite thoroughly studied; the other two are only briefly described. We have synthesized seven esters of levulinic acid, namely, methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl and isoamyl levulinates, thus adding four new esters to the list already described. These esters were highly purified and a few of their important physical constants determined. To characterize them, we have also prepared the corresponding semicarbazones and phenylhydrazones. Their melting points and nitrogen contents were accurately determined.

Experimental

Preparation of Levulinic Acid.—Five hundred cc. of commercial concentrated hydrochloric acid was mixed in a 2-liter beaker with an equal volume of water. The acid solution was heated to boiling and 500 g. of commercial glucose (solid, technical lumps from E. Merck, Darmstadt) was added in small portions with constant stirring. The solution was boiled gently for ten minutes. After cooling, the large amount of humus material was filtered off by suction. The filtrate was transferred to a 3-liter round-bottomed flask and refluxed vigorously for at least twenty-four hours, in order to convert the intermediate product, oxymethylfurfural, to levulinic acid. The humus material further precipitated out was filtered off from time to time. The filtrate was distilled at atmospheric pressure until the thermometer registered at 125°. The hydrochloric acid solution thus recovered could be used over again. The residue, after filtration, was distilled under reduced pressure. The fraction boiling from 146 to 184° at 7 mm. pressure was collected and redistilled. Upon chilling, the practically colorless liquid solidified to large, glassy, shining crystals, m. p. 33–35°; b. p. 245–246°; b. p. 145° at 4 mm.; yield, about 150 g. from 1 kilo of glucose used. The acid was freely soluble in water, ethyl alcohol or ether.

Esterification.—The acid was esterified directly with excess of absolute alcohol (methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, or isoamyl) in the presence of a small amount of hydrochloric acid. The procedure described by Adkins and McElvain[5] for the preparation of ethyl benzoate was adopted. The yield was about 65% of the theoretical. The tables show the simple physical constants and the chemical analysis of the various esters prepared. These liquids, colorless and with faint pleasant odor, are insoluble in water (except methyl levulinate), soluble in alcohol, benzene or carbon bisulfide, and very soluble in ether, chloroform, carbon tetrachloride or ethyl acetate.

Preparation of Semicarbazones.—The procedure recommended by Baeyer[6] was followed. To a solution of semicarbazide hydrochloride of known strength, the calculated amount of potassium acetate in alcohol and the ester of levulinic acid were added.

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[4] (a) V. Grote, Kehrer and Tollens, *Ann.*, **206**, 220–222 (1881); (b) Conrad, *ibid.*, **188**, 225 (1877); (c) Michael, *J. prakt. Chem.*, [2] **44**, 114 (1891).

[5] Adkins and McElvain, "Practice of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1st ed., **1925**, p. 221.

[6] Baeyer, *Ber.*, **27**, 1918 (1894).

TABLE I

SIMPLE CONSTANTS OF ALKYL LEVULINATES

Levulinates	B. p., °C.	d_4^{20}	n_D^{20}	Molecular refraction Gladstone and Dale Obs.	Calcd.	Lorentz and Lorenz Obs.	Calcd.
Methyl	191–193	1.05113	1.4231	52.36	52.27	31.52	31.77
Ethyl	199–201	1.01336	1.4225	60.08	59.92	36.17	36.37
Isopropyl	203–205	0.98422	1.4220	67.79	67.57	40.83	40.97
n-Propyl	214–216	.98988	1.4255	67.96	67.57	40.88	40.97
Isobutyl	222–224	.97047	1.4264	75.63	75.22	45.48	45.57
n-Butyl	229–231	.97452	1.4290	75.77	75.22	45.53	45.57
Iso-amyl	238–240	.95921	1.4310	83.64	82.87	50.23	50.17

TABLE II

ANALYSIS OF ALKYL LEVULINATES

Alkyl	Formula	Hydrogen, % Calcd.	Found	Carbon, % Calcd.	Found	Saponification no. Calcd.	Found
Methyl	$C_6H_{10}O_3$	7.75	7.70	55.35	54.84	431.3	427.4
Ethyl	$C_7H_{12}O_3$	8.39	7.91	58.30	57.84	389.3	392.9
Isopropyl	$C_8H_{14}O_3$	8.92	8.60	60.72	60.45	354.8	357.9
Propyl	$C_8H_{14}O_3$	8.92	9.23	60.72	60.57	354.8	351.3
Isobutyl	$C_9H_{16}O_3$	9.37	9.00	62.75	62.59	325.9	324.7
Butyl	$C_9H_{16}O_3$	9.37	9.81	62.75	63.22	325.9	322.4
Isoamyl	$C_{10}H_{18}O_3$	9.74	10.14	64.47	64.12	301.4	297.5

The methyl and ethyl esters reacted very quickly. Their semicarbazones precipitated almost instantaneously upon shaking. The higher homologs were allowed to stand overnight, whereby beautiful crystals came out smoothly. They were white solids with definite crystalline structure, insoluble in water, only difficultly soluble in ether, carbon bisulfide or carbon tetrachloride, soluble in ethyl alcohol, ethyl acetate or benzene and very soluble in chloroform.

For analysis and melting point determinations, the pure crystals were filtered off by suction, washed with a small amount of distilled water and dried in a vacuum over sulfuric acid. The nitrogen content was found by the Dumas method.

TABLE III

MELTING POINTS AND ANALYSES OF SEMICARBAZONES

Alkyl	Formula	M. p., °C.	Subs., g.	N_2, cc.	*P*, mm. (corr.)	*T*, °C.	Nitrogen, % Calcd.	Found
Methyl	$C_7H_{13}N_3O_3$	142–143	0.0606	11.9	747.25	17.7	22.46	22.68
Ethyl	$C_8H_{15}N_3O_3$	147–148	.0422	7.4	749.54	11.0	20.89	20.79
Propyl	$C_9H_{17}N_3O_3$	129–130	.0620	10.8	736.3	17.0	19.53	19.87
Isopropyl	$C_9H_{17}N_3O_3$	141–142	.0470	8.1	736.7	21.0	19.53	19.40
Butyl	$C_{10}H_{19}N_3O_3$	102–103	.0512	8.4	737.1	19.0	18.34	18.61
Isobutyl	$C_{10}H_{19}N_3O_3$	112–113	.0520	8.3	740.1	15.0	18.34	18.43
Isoamyl	$C_{11}H_{21}N_3O_3$	91–92	.0610	9.5	737.6	16.0	17.28	17.86

Preparation of Phenylhydrazones.—The procedure described by Michael[4c] was followed. A saturated solution of phenylhydrazine hydrochloride was prepared by dissolving the hydrochloride in about twelve parts of water. A molecular equivalent of alkyl levulinate was then added to the solution. Upon shaking and then standing for a few hours, crystals of the hydrazones separated out. They were filtered off by suction, pressed between filter paper and then dried in a vacuum over sulfuric acid to constant weight. The crystals were colorless when freshly prepared. On exposure to air, they turned yellowish-brown, showing that they were unstable toward oxygen. For melting point determination and analysis, the compound must be freshly prepared and recrystallized from benzene. The hydrazones of alkyl levulinates were insoluble in water, soluble in ether, alcohol or carbon tetrachloride, and very soluble in benzene, carbon bisulfide, chloroform or ethyl acetate. Their nitrogen content was analyzed for by the Dumas method.

TABLE IV

MELTING POINTS AND ANALYSES OF PHENYLHYDRAZONES

Alkyl	Formula	M. p., °C.	Subs., g.	N_2, cc.	*P*, mm. (corr.)	*T*, °C.	Nitrogen, % Calcd.	Nitrogen, % Found
Methyl	$C_{12}H_{16}N_2O_2$	94–96	0.0322	3.7	738.2	18.0	12.73	13.10
Ethyl	$C_{13}H_{16}N_2O_2$	103–104	.1142	11.8	737.4	15.0	11.97	11.89
Propyl	$C_{14}H_{20}N_2O_2$	88–90	.0920	8.9	748.6	17.0	11.29	11.22
Isopropyl	$C_{14}H_{20}N_2O_2$	108–109	.0882	8.4	740.2	18.5	11.29	10.87
Butyl	$C_{15}H_{22}N_2O_2$	79–81	.1182	11.3	737.5	17.0	10.69	10.92
Isobutyl	$C_{15}H_{22}N_2O_2$	84–86	.1062	10.0	748.5	16.0	10.69	10.96
Isoamyl	$C_{16}H_{24}N_2O_2$	70–72	.0616	5.3	750.3	15.0	10.14	10.07

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Summary

1. A simple procedure for the preparation of levulinic acid from commercial glucose is described.

2. Seven alkyl levulinates (three previously described and four new compounds) have been synthesized by direct esterification of levulinic acid with various alcohols. The esters were obtained highly pure and their simple constants studied.

3. These esters were characterized by their corresponding semicarbazones and phenylhydrazones. Among these, only the ethyl derivatives were previously described.

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