Anal. Calcd. for $C_6H_{14}ON_2$: N, 21.52. Found: N, 21.79.

***dl*-Methylisopropylcarbinylamine Hydrochloride.**—Recrystallized from alcohol–ether, this forms tiny, felted needles, m. p. 216°.

Anal. Calcd. for $C_5H_{14}NCl$: N, 11.33. Found: N, 11.65.

***dl*-*s*-Butylcarbinyl Urea.**—This urea was prepared from *s*-butylcarbinylamine and nitrourea. The amine was obtained by a Hofmann reaction (using 10% excess sodium hypochlorite) on *s*-butylacetamide,[14] prepared by the Aschan method[8] from *s*-butylacetic acid.[14,15] The urea, recrystallized from water, forms small, pearly leaves, melting at 125°, and soluble in hot benzene, very soluble in alcohol, moderately soluble in ether, and soluble in hot water.

Anal. Calcd. for $C_6H_{14}ON_2$: N, 21.52. Found: N, 21.84.

***dl*-*s*-Butylcarbinylamine hydrochloride,** recrystallized from alcohol–ether, forms tiny, felted crystals, m. p. 180°.

Anal. Calcd. for $C_5H_{14}NCl$: N, 11.33. Found: N, 11.56.

1-Amyl Barbitals.—These compounds were all prepared in the customary manner (condensation of one mole of urea with one mole of ethyl diethylmalonate, in the presence of three moles sodium ethylate, the reaction lasting four and one-half hours). In general, they were worked up by dissolving the reaction product in water, acidifying, extracting with ether, and then extracting the barbituric acid from the ether with dilute sodium hydroxide solution. After saturation of the alkaline solution with carbon dioxide, the product was filtered off if solid or extracted with ether or hexane and the solvent evaporated. With the exception of the *n*-butylcarbinyl barbital and the methylpropylcarbinyl barbital, the products were recrystallized from aqueous alcohol until pure. The methylpropylcarbinyl barbital was first distilled (b. p. *ca.* 147° at 1.5 mm.) and then crystallized from pentane, while the *n*-butylcarbinyl barbital was crystallized from pentane, with or without a preliminary distillation under low pressure. Both these compounds must be manipulated, apart from distillation, at temperatures below 0° on account of their low melting points and extreme solubility.

The amyl barbitals are all white, crystalline compounds. They are practically insoluble in water, are soluble in cold 5% sodium hydroxide solution, and are very soluble in the usual organic solvents. With the exception of the two low-melting compounds, which have a slightly burning taste, followed by a bitter after-taste, the amyl barbitals are practically tasteless. Analytical data, etc., are recorded in Table I. Melting points are corrected. The microanalyses were carried out by Mr. W. S. Ide.

Complete pharmacological data will be published in another place. In the meantime, the minimum hypnotic and lethal doses (by intraperitoneal injection, using white mice) are given in Table I. There were secondary deaths with four of the compounds. In some cases, the effect is not purely hypnotic, in fact, *dl*-1-methylisopropylcarbinyl barbital is a convulsant. For comparison, the M. H. D. of barbital itself, determined in the same way, is 0.70–1.00 and the M. L. D. is 2.5.

(14) Bentley, *J. Chem. Soc.*, **67**, 264 (1895).
(15) Ehrlich, *Ber.*, **41**, 1453 (1908).

Summary

The preparation and properties of the eight isomeric amyl ureas and the corresponding eight 1-amyl barbitals are described, and the minimum hypnotic and the minimum lethal doses of the latter are given.

TUCKAHOE, NEW YORK RECEIVED OCTOBER 14, 1937

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Glycofuranosides and Thioglycofuranosides. II. Crystalline α-Ethylgalactofuranoside

BY JOHN W. GREEN AND EUGENE PACSU

In a recent publication[1] dealing with the preparation of crystalline β-ethylgalactofuranoside by a new method, it has been stated that "from the mother liquor a sirup is obtained, which may contain the unknown α-form, and which is being investigated." The ether extract of this sirup, on standing in the ice box for several months, deposited a crystalline material in the form of hard glassy buttons. After crystallization from ethyl acetate, the product had the appearance of short needles, with m. p. 139–140° and $[\alpha]^{20}D$ 92° in water solution.

(1) Green and Pacsu, THIS JOURNAL, **59**, 1205 (1937).

It can now be stated that this substance represents the hitherto unknown α-isomer of the β-ethylgalactofuranoside ($[\alpha]^{20}D$ −102° in water solution). This conclusion has been arrived at from the results of the analysis and the rate of hydrolysis of the compound and from the fact that the rotational difference (194°) of the two isomers agrees closely with that (193.5°) of the two ethylgalactopyranosides ($[\alpha]^{20}D$ 186.8° for the α-, and −6.7° for the β-pyranoside).

By the preparation of this new glycoside in pure state, a second pair of crystalline furanosides has become known in sugar chemistry, the first

pair being Haworth's ethylglucofuranosides.[2] The new α-furanoside, similar to the α-ethylglucofuranoside but unlike the corresponding β-isomers, is not hygroscopic and crystallizes readily from its solvents. It can be isolated in about 2% yield, as a by-product of the main reaction, which gives rise to the β-isomer.

Experimental

Preparation of α-Ethylgalactofuranoside.—To a solution of 28 g. of galactose ethylmercaptal in 250 cc. of absolute ethyl alcohol at 70°, 35 g. of yellow mercuric oxide and 10 g. of powdered drierite were added. The mixture was stirred rapidly, while a solution of 35 g. of mercuric chloride in 150 cc. of absolute ethyl alcohol was added over a period of thirty to forty minutes. After the reaction mixture cooled down to 30° in one hour, it was filtered and 10 cc. of pyridine was added to the filtrate, which was then kept at 0° overnight. After the pyridine–mercuric chloride compound was filtered off, the filtrate was evaporated *in vacuo* at 40° to a sirup, which was dissolved in 100 cc. of water, the solution neutralized with dilute alkali to phenolphthalein, then evaporated to a sirup at 50° *in vacuo*. For removal of water, the substance was taken up in absolute alcohol and the solution evaporated to a thick sirup. This was dissolved in 500 cc. of boiling ethyl acetate, the solution cooled to room temperature, then decanted from oily drops and seeded with β-ethylgalactofuranoside. The crystallization of the β-compound was completed at 0°; yield 10 g. The mother liquor was evaporated to 200 cc. and kept in the ice box for a prolonged time. After several days usually some more β-crystals were precipitated, and possibly some α-crystals, too. The latter were separated mechanically from the β-crystals, as their appearance was that of round translucent buttons, while the β-isomer crystallized in white fragile needles. In some experiments only β-crystals were formed and from the mother liquor, after filtration, the α-compound precipitated as small round buttons all over the wall of the flask. In either case, the crude product ($[\alpha]^{20}D$ 84°) was dissolved in about 100 times its weight of hot ethyl acetate, and, on cooling to room temperature, the solution deposited the pure α-ethylgalactofuranoside in the form of beautiful short needles; yield about 0.40 g.; m. p. 139–140°; $[\alpha]^{20}D$ 92° (0.0500 g. substance, 4 cc. of water solution, 2-dm. semi-micro tube, rotation 2.30° to the right). The substance was devoid of action toward boiling Fehling's solution.

For the determination of the rate of hydrolysis, 0.1087 g. of the substance was dissolved in 20 cc. of hot water, the solution was quickly mixed with 5 cc. of hot 0.05 *N* hydrochloric acid ($t = 0$) and replaced in the boiling water-bath. At intervals of twelve, eighteen, and thirty minutes, respectively, 5-cc. portions were removed and analyzed for free galactose (found: 11.45, 14.25, and 18.33 mg., respectively; calcd. for complete hydrolysis: 18.81 mg.) according to the method of Bertrand. From these data, the average value of $k \times 10^5 = 8000$, calculated from the unimolecular law, was obtained.

Anal. Calcd. for $C_8H_{16}O_6$: C, 46.15; H, 7.75. Found: C, 45.96, 46.23; H, 7.87, 7.90.

(2) Haworth and Porter, *J. Chem. Soc.*, 2796 (1929); Haworth, Porter and Waine, *ibid.*, 2254 (1932).

Summary

α-Ethylgalactofuranoside has been isolated in the crystalline state. Its specific rotation in water solution, 92°, checks with Hudson's rules of isorotation. The rate of hydrolysis in aqueous acid is of the order given by furanosides.

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[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

Derivatives of Piperazine. XIII. Analogs of Ephedrine Containing the N-Phenylpiperazine Nucleus

BY BURT L. HAMPTON AND C. B. POLLARD

The effect of several reducing agents on certain of the α-amino ketones derived from N-phenylpiperazine, which have been reported previously by us,[1] forms the basis of this paper. It was desired to prepare certain amino alcohols which were similar in structure to ephedrine and related compounds and which contained the N-phenylpiperazine nucleus. We have been successful in reducing two of these ketones, N-phenyl-N′-phenacylpiperazine, and N-phenyl-N′-*p*-methylphenacylpiperazine, to the corresponding secondary alcohols. Other reductions were not attempted at this time.

The success of this reduction is of interest because of the fact the nitrogen atom is heavily loaded, and, generally, when this is the case most reducing agents tend to split the molecule.

The reduction of N-phenyl-N′-phenacylpiperazine with aluminum amalgam in neutral solution gave N-phenylpiperazine and acetophenone. On reduction with hydrazine in a sealed tube at 185–195° N-phenylpiperazine was the only product isolated and identified, although a strong odor of

(1) Hampton and Pollard, THIS JOURNAL, **59**, 2446 (1937).