TABLE I

Starting material	Chlorinating agent	Solvent	Conditions	Reaction product	Yield, g.	B.p., °C.	Mm.
$(CH_3O{\cdot}C_6H_4{\cdot}PS_2)_2$							
68 g.	Excess Cl_2	300 cc. CCl_4	8 hr. room temp., 8 hr. SO_2	$CH_3O{\cdot}C_6H_4{\cdot}POCl_2$[a]	63	149–153	6–7
91.7 g.	32 g. Cl_2	50 cc. CCl_4	16 hr. room temp.	$CH_3O{\cdot}C_6H_4{\cdot}PSCl_2$	92.7	124–128	1
11 g.	14 g. PCl_5	50 cc. $POCl_3$	1 hr. reflux, then SO_2	Same[b]	8.8	155–157	8
10 g.	6.6 cc. SO_2Cl_2	50 cc. CCl_4	Room temp.	Same	7.5	156–157	8
18.5 g.	67.5 g. S_2Cl_2[c]	50 cc. CCl_4	5 hr. reflux	Same	19.9		
$(C_{10}H_7PS_2)_2$							
12.15 g.	Cl_2 until sol.	75 cc. CCl_4	Room temp.	$C_{10}H_7{\cdot}PSCl_2$[d]	13.2	173–174	4
$(C_6H_5PS_2)_2 + P_4S_7$							
7.0 g.	13.0 g. PCl_5	50 cc. $POCl_3$	2 hr. reflux	$C_6H_5PSCl_2$[e]	5.5	120	12
$C_6H_5PSCl_2$							
12.0 g.	Excess Cl_2	25 cc. CCl_4	Room temp., then SO_2	$C_6H_5POCl_2$[f]	8.1	105–106	5

[a] *Anal.* Calcd. for $C_7H_7O_2Cl_2P$: C, 37.3; H, 3.1; Cl, 31.5; S, 0.0. Found: C, 36.6, 36.7; H, 3.23, 3.23; Cl, 31.5; S, 0.46. [b] *Anal.* Calcd. for $C_7H_7Cl_2OPS$: C, 34.8; H, 2.9; Cl, 29.4; S, 13.25. Found: C, 34.3; H, 2.81; Cl, 29.2; S, 13.1. [c] In a separate experiment it was determined that sulfur monochloride does not further chlorinate the phosphonothioic dichloride. The latter was heated to reflux for five hours with an excess of sulfur monochloride; 87% of the phosphonothioic dichloride was recovered by distillation under reduced pressure and only a negligible amount of sulfur was detected. [d] *Anal.* Calcd. for $C_{10}H_7Cl_2PS$: C, 46.0; H, 2.68; Cl, 27.2; P, 11.9; S, 12.4. Found: C, 45.2; H, 2.57; P. 11.7; S, 10.2; Cl, 28.7. [e] *Anal.* Calcd. for $C_6H_5Cl_2PS$: C, 34.1; H, 2.36; Cl, 33.6; P, 14.7; S, 15.18. Found: C, 33.8; H, 2.55; Cl, 33.8; P, 16.03; S, 14.3. [f] *Anal.* Calcd. for $C_6H_5Cl_2OP$: C, 36.9; H, 2.56; Cl, 36.4; P, 15.90. Found: C, 37.2; H, 2.80; Cl, 36.4, 36.7; P, 17.17.

44.4 g. (0.1 mole) of P_4S_{10} were heated in a 1-l. stainless steel shaking autoclave at 185° for 24 hours. The contents consisted of a yellow solid and an orange-brown liquid. Water, 150 cc., was added gradually. Since this hydrolysis is slow, the mixture was refluxed for 42 hours. The bulk of the organic layer was decanted off. The remaining mixture was reheated, the water layer adjusted to a volume of about 500 cc. and the rest of the xylene layer separated. The hot aqueous solution was treated with decolorizing carbon, clarified and cooled. *o*-Xylylphosphonic acid, 35.5 g., m.p. 149–152°, crystallized out. It was identical with the phosphonic acid previously obtained from xylene and phosphoric anhydride. The m.p. of the pure acid is 153–153.5°. From the aqueous mother liquor a pure phosphonic acid could not be isolated.

Reaction of 2-Isopropylnaphthalene with Phosphorus Pentasulfide. 2-Isopropyl-x-naphthylphosphonic Acid.—179 g. (1 mole) of 95% 2-isopropylnaphthalene and 44.4 g. (0.1 mole) of P_4S_{10} were heated with stirring at 170–175° for 18 hours. Hydrogen sulfide was evolved and the phosphorus sulfide which dissolved produced an orange-brown solution. The charge was cooled to 80° and 50 cc. of water was cautiously added. Hydrolysis was accomplished by refluxing for 20 hours. The layers were separated hot. The (water-insoluble) phosphonic acid crystallized from the organic layer, was filtered and washed with benzene; yield 11.0 g. of crude product, m.p. 210–212° after recrystallization from 80% alcohol.

Anal. Calcd. for $C_{13}H_{15}O_3P$: C, 62.4; H, 6.0; P, 12.4; neut. equiv., first break, 250, second break, 125. Found: C, 61.8; H, 5.66; P, 13.29, 13.14; neut. equiv., first break, 240.7, second break, 117. The sample was not quite pure.

The 2-isopropyl-x-naphthylphosphonic acid has considerable wetting power, but forms insoluble calcium and magnesium salts.

Chlorination Experiments.—These are summarized in Table 1.

In these reactions sulfur is removed as elemental sulfur when sulfur monochloride is used. When phosphorus pentachloride is used, thiophosphoryl chloride is formed. When chlorine, sulfur dichloride or sulfuryl chloride are employed, it depends upon the ratio of the reactants whether the removed sulfur appears as such or as sulfur mono- or dichloride; in the case of sulfuryl chloride, sulfur dioxide and thionyl chloride are formed. These inorganic chlorides boil much lower than the desired organophosphorus compounds and are easily removed by distillation.

BOUND BROOK, NEW JERSEY

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE A. M. TODD CO.]

A New Ketone from Oil of *Mentha rotundifolia*

BY ROBERT H. REITSEMA

RECEIVED APRIL 9, 1956

A new ketone has been isolated from oil of *Mentha rotundifolia*. The structure of 1,2-epoxypulegone (piperitenone oxide) is proposed on the basis of spectra and degradation work. It is indicated that this ketone is the same as has been isolated from Indian "spearmint" and from species of *Lippia* oils. Previous conversions of the material have been reinterpreted by the use of the new structure.

Over half of the essential oil from *Mentha rotundifolia* has been found to consist of an unusual terpene, $C_{10}H_{14}O_2$.[1] Isolation of the ketone by freezing, or by preparation of the semicarbazone, was possible either from the whole oil or from fractions rich in the material. Interesting properties of hybrids from *M. rotundifolia* crossed to other mint species made the study of this new compound valuable.

Although this is an unusual terpene in an essential oil, one with the same analysis, designated lippione, has been isolated from *Lippia* genus oils.[2] More recently another report has appeared indicating the

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[1] R. H. Reitsema, *J. Am. Pharm. Assoc.* (*Sci. Ed.*), **43**, 414 (1954).

[2] G. A. Fester, E. A. Martinuzzi and A. I. Ricciardi, *Rev. fac. ing. quim.* (*Sante Fe, Arg.*), **20**, 43 (1951), *Anal. assoc. quim. Argentina*, **42**, 43 (1954).

presence of an aldehyde with the same empirical formula in Indian "spearmint," *M. viridis*.[3] Since the nomenclature of the mint family is not uniform it was possible that *M. rotundifolia* was the same as *M. viridis*.[4] A comparison of the physical properties of the products isolated from the three sources is given in Table I.

TABLE I

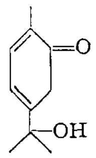
PROPERTIES OF THE TERPENE FROM THREE OILS

	M rotundifolia	*L. turbinata*[2]	*M. viridis*[3]
M. p., °C.	25.5–26		22.6 (cong.)
n_D (t, °C.)	1.5052 (28)		1.5050 (29)
$[\alpha]_D$	+150.6°	+156.7°	+181.3° (alc.)
d_4 (t, °C.)		1.0497 (22)	1.048 (30)
Mol. wt.			164 ± 5[a]
λ_{max}^{alc}	262 mμ (log ε 4.0)	262 mμ (log ε 4.04)	260 mμ (log ε 4.01)
Semicarbazone			
M.p., °C.	177.5–178	179 ± 3	175
$[\alpha]_D$	+176.5°[b]	+208°[b]	
Mol. wt.		216[c]	
λ_{max}^{alc}	274.5 mμ (log ε 4.06)	274.5 mμ (log ε 4.07)	250 mμ (log ε 4.04)

[a] Theory is 166. [b] 0.5% solution in chloroform. [c] Theory is 223.

The agreement of the physical constants of the three materials is satisfactory. There are enough specific characteristics in close agreement to make confusion of different materials unlikely on this basis alone. The ultraviolet absorption, optical rotation and specific gravity are peculiar to this material and are not duplicated by other known terpene ketones. Some variation in melting point of the semicarbazone is likely since slight operational differences can alter the melting point.[2] Variation in ultraviolet absorption of the semicarbazone is possible also. The 274.5 mμ peak disappears and a new shoulder appears at about 230 mμ after two minutes in boiling ethanol. Intermediate curves can be obtained under less severe conditions. The semicarbazones from *M. rotundifolia* and *L. turbinata* showed no mixed melting point depression.

The compound from *L. turbinata* had been assigned structure I,[2] although this has no asymmetric center and the terpene actually has high optical activity. Structure II suggested for the *M. viridis* aldehyde did not seem completely satisfactory. The assignment of the 9.9 μ infrared absorption to the cyclopropane ring is not conclusive since many terpenes themselves show significant absorption in this region.[5] It is now proposed that the material is 1,2-epoxypulegone (III) which also can be considered as *d*-piperitenone oxide.



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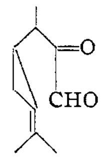

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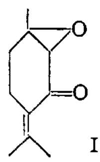
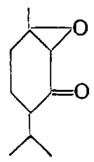


III

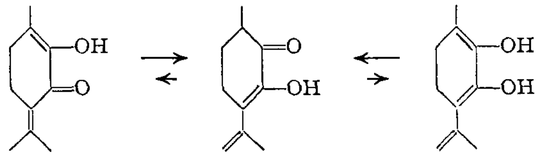


IV

Steam distillation of the ketone, or its semicarbazone, from dilute acid gave a new material, diosphenolene (V), m.p. 74.5°. The similarity of this acid reaction to that of piperitone oxide (IV) isolated from oil of a related mint species[6] was striking. The compound corresponds to the material $C_{10}H_{14}O_2$ from the previous report of Fester.[2] The positive reaction of the material with ferric chloride, periodate and silver nitrate, and its solubility and sublimation properties suggested a similarity to diosphenol. Catalytic reduction actually gave diosphenol, m.p. 82°. This indicated a *p*-menthane ring for the ketone.

A double bond conjugated with a carbonyl group was indicated by strong infrared absorption at 1665 and 1595 cm.$^{-1}$. The infrared absorption at 840 cm.$^{-1}$ was in agreement with postulation of an isopropylidene group.[7] It has been well established that the ketone and some of its derivatives gave acetone by ozonolysis or permanganate oxidation.[2,3] Thus, the unsaturation is placed between carbons 4 and 8. The ultraviolet absorption at 262 mμ is about 8 mμ higher than calculated, but the effect of the adjacent epoxide group and of the stereoisomeric configuration is not certain and is being studied. The absorption of the semicarbazone at 274.5 mμ is at the longer wave length of the normal range of semicarbazones of α,β-unsaturated ketones, perhaps reflecting the same bathochromic shift.

The evidence for the ether group is by inference. No indications of a second carbonyl or a hydroxyl group were obtained. Negative ferric chloride and slow positive periodate tests on the ketone, facile reaction with acid, and addition of isopropyl alcohol during Meerwein–Pondorf reduction all suggested the epoxide structure. Although other points of attachment of the second ether bond are possible and all other type bonds have not been eliminated, the formation of diosphenolene and not an aromatic compound or one with a new isolated double bond indicated the appropriateness of the 1,2-epoxide group.



Va Vb Vc

Diosphenolene produced by acid treatment of the ketone or of the semicarbazone would then be 3,8(9)-*p*-menthadiene-3-ol-2-one (Vb). Other structures, such as Va and Vc, are possible but consideration of the main absorption at 305.5–308 mμ would

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[3] K. K. Chakravarti and S. C. Bhattacharyya, *Perfumery Essent. Oil Record*, **46**, 256 (1954).

[4] Plant material used in the present study has been carefully identified and grown in our own fields under the direction of M. J. Murray. Specimens of the plants have been deposited with the St. Louis Botanical Gardens and the Cornell University Herbarium.

[5] A. T. O'Connor and L. A. Goldblatt, *Anal. Chem.*, **26**, 1726 (1954).

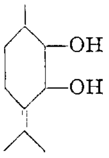
[6] R. H. Reitsema and V. J. Varnis, THIS JOURNAL, **78**, 3792 (1956).

[7] D. Barnard, L. Bateman, A. J. Harding, H. P. Kock, N. Sheppard and G. B. B. M. Sutherland, *J. Chem. Soc.*, 915 (1950).

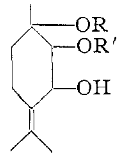
indicate the complete conjugated structure.[8] A shoulder at about 274 mμ which could not be eliminated in earlier work[2] may be due to the contribution of other tautomeric forms such as in diosphenol.

The degradation products, previously reported, failed to give real evidence of the structure of the ketone. Oxalic acid, acetone and α-hydroxyisobutyric acid[2] are products anticipated from structure III as well as from several others. Formation of α-methylglutaric acid by ozonolysis followed by hypobromite reaction[3] can be explained by assuming the ozonolysis to be preceded by an acid-catalyzed opening of the epoxide ring to Vb followed by the normal oxidation reactions.

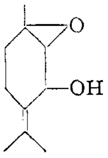
Reductions of the ketone observed earlier can be explained with the new structures. Lithium aluminum hydride reduction gave presumably a diol, $C_{10}H_{18}O_2$, m.p. 148°,[3] which would correspond to 2,3-dihydroxy-4,8-*p*-menthene (VI) and the positive periodate test and formation of acetone by ozonolysis would be normal.[9] Reduction with aluminum isopropoxide gave a product, m.p. 122°,[3] which would correspond to VII or VIII. A positive periodate test indicated the reasonableness of VII. The diol also isolated from the reduction would correspond perhaps to the epoxy alcohol IX.



VI

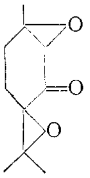


VII, R = $CH(CH_3)_2$; R′ = H
VIII, R = H; R′ = $CH(CH_3)_2$

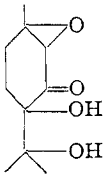


IX

The epoxide of the ketone, prepared[3] by coincidence, would be 1,2,4,8-diepoxymenthone (piperitenone dioxide) (X) m.p. 80°. No acetone or formaldehyde was obtained on attempted ozonolysis of this material. Sulfuric acid (2%) at room temperature gave cleavage of one oxide group with formation of a compound which could then be 4,8-dihydroxy-1,2-epoxymenthone, $C_{10}H_{16}O_4$ (XI). This material gave negative ferric chloride and tetranitromethane tests and positive Fehling and silver nitrate tests, indicating that the original 1,2-epoxide group is still intact. This is in accord with the behavior of piperitenone oxide (III) which failed to react readily with 5% sulfuric acid at room temperature and required heat.



X



XI

The epoxyketones, piperitone oxide and piperitenone oxide, are of interest in the biochemistry of constituents of mint species, but they do not appear to be closely allied with early formation of the oxygenated materials.

Acknowledgment.—The technical assistance of Mr. Wm. Faas and Mr. V. J. Varnis and permission of the A. M. Todd Co. to publish this data are gratefully acknowledged.

Experimental[10]

Isolation of *M. rotundifolia* Ketone.—*M. rotundifolia* plants grown in the vicinity of Kalamazoo, Michigan, were steam distilled and the oil carefully separated from the condensate liquid. The oil was a vesicant, and assayed 51% ketones as $C_{10}H_{14}O_2$ by the cold oximation method; $n^{20}\text{D}$ 1.5026, αD 65.4°. Freezing a sample of the oil in a refrigerator at 2–4° gave some solid from which the uncongealed oil was decanted. The solid was washed with cold hexane three times and recrystallized from a small amount of hexane giving a white solid, m.p. 25.5–26°, $n^{18}\text{D}$ 1.5052, $[\alpha]^{25}\text{D}$ 150.6° (*c* 10.2, hexane); $\lambda_{\max}^{\text{EtOH}}$ 262 mμ (ε 10,000); negative Fehling, periodate and ferric chloride tests initially; after standing, positive periodate and Fehling tests.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.57; H, 8.81.

Semicarbazone of *M. rotundifolia* Ketone.—A mixture of 10.0 g. of *M. rotundifolia* oil, 8.0 g. of semicarbazide hydrochloride and 6.0 g. of anhydrous sodium acetate was stirred vigorously with 100 ml. of water and 50 ml. of ethanol. After one hour the solution had turned yellow and a solid had appeared. After standing overnight in the refrigerator, and after filtration of the crystals, the air-dried product, m. 176–179° (with sintering from 162), weighed 10.1 g. Recrystallization from ethanol gave a white solid, m.p. 177.5–178°, $[\alpha]^{25}\text{D}$ 176.5° (*c* 0.5, alc.); $\lambda_{\max}^{\text{EtOH}}$ 274.5 mμ (ε 10,700). Some decomposition was apparent during prolonged heating during the recrystallization process at temperatures above 50°.

Anal. Calcd. for $C_{11}H_{17}O_2N_3$: C, 59.17; H, 7.68; N, 18.82. Found: C, 59.27; H, 7.42; N, 18.43.

The semicarbazone could be prepared equally well from fractions of the oil boiling at 70–76° at 3 mm. The mixed melting point of the semicarbazone with a sample of semicarbazone from *L. turbinata* provided by Dr. Fester, m.p. 178–180°, melted at 178–179°.

The dinitrophenylhydrazone could be isolated in the crude state, but it decomposed during attempted recrystallization.

***M. rotundifolia* Ketone Reduction.**—Catalytic reduction of the ketone in ethanol with platinum oxide catalyst did not show any selective hydrogen uptake. The rotation and ultraviolet absorption taken on samples corresponding approximately to one and two equivalents of hydrogen were, respectively: 41.0° (*c* 1.33, EtOH), 255 mμ (ε 6,600); and −15.9° (*c* 0.627, EtOH), 250 mμ (ε 2,640). Chromatography suggested the presence of a new saturated ketone in addition to other ketones. The semicarbazone of the product, m.p. 214–215°, $\lambda_{\max}^{\text{EtOH}}$ 265 mμ (ε 22,900), was not analytically pure yet.

Previously the reduction had been reported[2] to give a product αD −23.9° whose semicarbazone melted at 217°, $\lambda_{\max}^{\text{EtOH}}$ 255.5 mμ (ε 12,890). The microanalysis of this derivative had led to the suggestion that a saturated monooxy ketone, probably carvomenthone, was present.

Diosphenolene (V).—Piperitenone oxide (1.12 g.) isolated by freezing the oil of *M. rotundifolia* and washing the solid with cold hexane was steam distilled from 50 ml. of 10% sulfuric acid. The distillate was cooled and filtered giving 0.49 (44%) of air-dried white crystals. Similarly, 9.56 g. of *M. rotundifolia* semicarbazone recrystallized from methanol, $[\alpha]^{25}\text{D}$ 171°, gave on similar distillation 2.82 g. (41%) of diosphenolene after recrystallization from 50% ethanol. A sample sublimed at atmospheric pressure melted at 73.5–74.5°, $\lambda_{\max}^{\text{EtOH}}$ 308 mμ (ε 8,400) [reported[2] m.p. 75.5°, $\lambda_{\max}^{\text{EtOH}}$

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[8] The absorption at 308 mμ is in agreement with the calculated shift from diosphenol at 274 mμ due to the additional double bond extending the conjugation. The structure proposed for the predominant form of diosphenolene is based upon this interpretation of its ultraviolet absorption spectrum by R. H. Eastman, Stanford University.

[9] Compare R. F. Nystrom and W. G. Brown, THIS JOURNAL, **70**, 3738 (1948).

[10] Unbracketed αD is used for observed rotations on homogeneous material taken without solvent at room temperature in a 1 decimeter tube. Ultraviolet absorptions were taken on a model DU Beckman spectrophotometer in 95% ethanol. Infrared analyses by Anderson Physical Laboratories, Champaign, Ill. Microanalyses by Clark Microanalytical Laboratory, Urbana, Ill.

305.5 mμ (ε 10,000)]. It gave a nearly black ferric chloride test and positive Fehling, periodate and silver nitrate tests. The decomposition of the ketone with dilute sulfuric acid was slow at room temperature and could be followed conveniently over a period of three days by loss of optical activity. This relative stability at moderate temperatures gives basis for postulating the split of only one of the oxide groups of the dioxide X at room temperature.

Diosphenolene Reduction. Diosphenol.—The reduction of 0.81 g. of diosphenolene recrystallized three times from ethanol or methanol in 10 ml. of ethanol using prereduced platinum oxide catalyst proceeded rapidly at room temperature. After 1.1 equivalents of hydrogen had been absorbed, the solution was filtered to remove catalyst, and water was added until the filtrate was cloudy. The white needles which appeared in the cold filtrate were separated and dried to constant weight at atmospheric pressure giving 0.25 g. (31%) of diosphenol, m.p. 80–81°. By sublimation from a bath at 80° at atmospheric pressure it was possible to obtain material, m.p. 83–83.5°, which failed to give a melting point depression when mixed with authentic diosphenol. An additional 7% of product, m.p. 63–66°, which was separated from the reaction mixture was presumably a mixture of diosphenol and diosphenolene. The ultraviolet absorption spectrum of the main product showed a single maximum at 274 mμ (ε 9,540) corresponding to authentic diosphenol of comparable purity, $\lambda_{\max}^{\mathrm{EtOH}}$ 272.5 mμ (ε 9,880). Ease of sublimation of the product and color with ferric chloride were identical to authentic diosphenol.

KALAMAZOO, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Derivatives of D-*gluco*-Dialdohexose

BY D. L. MACDONALD AND HERMANN O. L. FISCHER

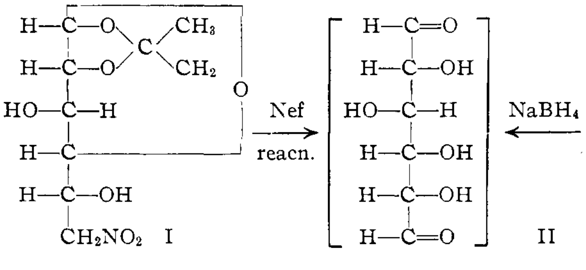
RECEIVED MAY 25, 1956

D-*gluco*-Dialdohexose isolated as its tetraethyl bis-mercaptal, has been prepared by the controlled reduction of D-glucuronolactone by means of sodium borohydride. This compound can also be obtained by carrying out a Nef reaction on 1,2-*O*-isopropylidene-6-deoxy-6-nitro-D-glucose.

Recently, interest in the dialdohexose type of sugar has been renewed, with the preparation of derivatives of D-*manno*-dialdohexose by oxidation of appropriately substituted derivatives of D-inositol[1] and of derivatives of *galacto*-dialdohexose by catalytic reduction of tetra-O-acetylmucyl dichloride.[2] A number of other substituted dialdoses have been reported in the literature,[1,2] but as yet no derivatives of a dialdose with the D-*gluco* configuration have been described.

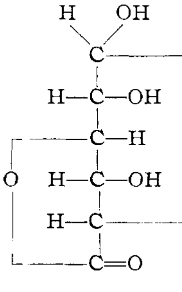
Chemically, D-*gluco*-dialdohexose is intermediate between D-glucose and D-glucuronic acid in its state of oxidation. Lindberg and Theander[3] have reported that oxidation of methyl β-D-glucopyranoside with dichromate gave a methyl glycoside of D-*gluco*-dialdohexose in very low yield, but the material was isolated as an impure sirup, and no crystalline derivatives amenable to structure proof were prepared. In a like manner, a derivative of D-*gluco*-dialdohexose may be an intermediate in the enzymatic oxidation of uridine diphosphate glucose to uridine diphosphate glucuronic acid. This enzyme preparation was obtained from a water extract of calf liver acetone powder, and catalyzed the aforementioned oxidation with concomitant reduction of two molar equivalents of diphosphopyridine nucleotide.[4] However, all attempts to demonstrate the expected intermediate dialdose derivatives were unsuccessful. Inasmuch as the D-*gluco*-dialdohexose may possibly have some real biological significance, we have attempted to prepare this compound and this communication deals with the preparation of a derivative of it using two distinctly different approaches, namely, oxidation of a D-glucose derivative and reduction of D-glucuronolactone.

Grosheintz and Fischer[5] prepared a mixture of 1,2-*O*-isopropylidene-6-deoxy-6-nitro-D-glucose and 1,2-*O*-isopropylidene-6-deoxy-6-nitro-L-idose from 1,2-*O*-isopropylidene-D-*xylo*-dialdopentose and nitromethane and separated the products by preferential acetonation of the L-idose isomer. By the use of the Nef reaction,[6] the 1,2-*O*-isopropylidene-6-deoxy-6-nitro-D-glucose (I) has been converted into D-*gluco*-dialdohexose (II), which was isolated from the aqueous solution as its insoluble crystalline tetraethyl bis-mercaptal in a yield of 47%. This derivative was further characterized as its crystalline tetraacetate.



I

II



III

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[1] C. E. Ballou and H. O. L. Fischer, THIS JOURNAL, **75**, 3673, 4695 (1953).

[2] M. L. Wolfrom and E. Usdin, *ibid.*, **75**, 4318 (1953).

[3] B. Lindberg and O. Theander, *Acta Chem. Scand.*, **8**, 1870 (1954).

[4] J. L. Strominger, H. M. Kalckar, J. Axelrod and E. S. Maxwell, THIS JOURNAL, **76**, 6411 (1954).

[5] J. M. Grosheintz and H. O. L. Fischer, *ibid.*, **70**, 1476 (1948).

[6] J. U. Nef, *Ann.*, **280**, 263 (1894); J. C. Sowden, *Advances in Carbohydrate Chem.*, **6**, 291 (1951).