from ethanol, m.p. 208–210° dec. (reported 212–213° (vac.),[2] 210–211°,[3,4] 208–209°,[1] 207–208°[6]); $[\alpha]^{24}\text{D}$ +160.4° (c 1.92, chloroform) (reported $[\alpha]^{22}\text{D}$ +162.3°,[5] $[\alpha]^{25}\text{D}$ 150.3°,[3] $[\alpha]^{18}\text{D}$ +165.8°[2]).

Anal. Calcd. for $C_{18}H_{21}NO_5$: C, 65.24; H, 6.39; N, 4.23. Found: C, 65.20, H, 6.52; N, 4.20.

The ultraviolet absorption spectrum in ethanol shows λ_{max} 242 mμ (log ϵ 3.69), λ_{max} 295 mμ (log ϵ 3.65), λ_{min} 262 mμ (log ϵ 2.62).

Tazettine Picrate.—Prepared in aqueous ethanol and recrystallized from ethanol, the picrate formed yellow prisms, m.p. 211–213° dec. (reported 192°[1,12] 205–208°,[4] 213°[6]).

Anal. Calcd. for $C_{24}H_{24}N_4O_{12}$: C, 51.43; H, 4.32; N, 10.00. Found: C, 51.35; H, 4.47; N, 9.95.

Tazettine Methiodide.—Prepared in ethanol and recrystallized three times from ethanol, the methiodide formed colorless prisms, m.p. 223–224° dec. (reported 238°,[1] 220° dec.,[3] 220–223°,[4] 211–213° dec.[6])

Anal. Calcd. for $C_{19}H_{24}NO_5I\cdot{}^1/_2H_2O$: C, 47.31; H, 5.22; N, 2.90. Found: C, 47.44; H, 5.20; N, 2.78.

Tazettine Methopicrate.—A solution of 0.114 g. of tazettine methiodide in 5 ml. of water was treated with aqueous picric acid until no further precipitation occurred. The precipitate was recrystallized from aqueous ethanol, 0.105 g., m.p. 237–239° dec. (reported[6] 234° dec.).

Anal. Calcd. for $C_{25}H_{26}N_4O_{12}$: C, 52.26; H, 4.56; N, 9.75. Found: C, 52.23; H, 4.70; N, 9.90.

Tazettine Acetate.—A solution of 0.659 g. of tazettine, 3 ml. of pyridine and 1 ml. of acetic anhydride was refluxed for one hour. The solution was concentrated, dissolved in chloroform and washed once with 5% sodium carbonate solution and once with water, dried and concentrated to a viscous oil that would not crystallize. The oil was chromatographed on 30.0 g. of alumina. Elution with benzene gave 252 mg. of oil that crystallized on trituration with ethyl acetate, m.p. 119–122°. The solid was recrystallized twice from aqueous methanol, 185 mg., m.p. 124–126° (reported 125–126.5°,[3] 124–125°[1]).

Anal. Calcd. for $C_{20}H_{23}NO_6$: C, 64.33; H, 6.21; N, 3.75. Found: C, 64.45; H, 6.32; N, 3.51.

Purification of Lycorine.—An aqueous suspension of 300 mg. of crude lycorine was acidified with dilute hydrochloric acid. The precipitated lycorine hydrochloride was dissolved by heat and the brown solution was decolorized with Darco. Upon cooling, 295 mg. of **lycorine hydrochloride monohydrate** crystallized as colorless elongated prisms, m.p. 213–215° (reported 206°,[15] 216°,[7] 228–234° dec.,[13] 258° dec.[14]); $[\alpha]^{27}\text{D}$ +45.7° (c 0.34, water) (reported $[\alpha]^{18}\text{D}$ +40.5°,[13] $[\alpha]^{9}\text{D}$ +96.8°,[14] $[\alpha]\text{D}$ +43°[15]).

Anal. Calcd. for $C_{16}H_{20}NO_5Cl$: C, 56.22; H, 5.90; N, 4.10. Found: C, 55.96; H, 5.66; N, 4.33.

When a solution of 295 mg. of this hydrochloride was made basic, 214 mg. of lycorine, m.p. 247–252° dec., was precipitated. Two recrystallizations from pyridine gave colorless prisms, m.p. 250–255° dec.[16] (reported 266–267° dec.,[17] 270° dec.,[13] 275° dec.,[18] 277°[7]); $[\alpha]^{27}\text{D}$ −75.1° (c 0.16, abs. ethanol) (reported $[\alpha]^{21}\text{D}$ −76°,[13] $[\alpha]^{10}\text{D}$ −95.8°,[17] $[\alpha]^{13}\text{D}$ −123.7°,[18] $[\alpha]^{2}\text{D}$ −120°[15]).

Anal. Calcd. for $C_{16}H_{17}NO_4$: C, 66.88; H, 5.96; N, 4.88. Found: C, 66.57; H, 6.16; N, 4.77.

Dihydrolycorine.—To a suspension of platinum, prepared by the atmospheric hydrogenation of 100 mg. of platinum oxide in 5 ml. of glacial acetic acid, was added a solution of 1.33 mmoles of lycorine in 10 ml. of glacial acetic acid. The reduction stopped when 107% of the theoretical amount of hydrogen had been absorbed. The catalyst was separated by filtration and the acetic acid was removed under an air jet. The residue was dissolved in water and made basic with 10% sodium carbonate solution. The precipitated dihydro base, 351 mg., m.p. 230–237° dec., was recrystallized from pyridine–ethanol (1:4) to give 237 mg. of pure base, m.p. 236–237° dec. (reported[15] 247°).

Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.56; H, 6.47; N, 5.02.

Lycorine Diacetate.—By the procedure of Reichstein,[13] 100 mg. of lycorine gave 71 mg. of lycorine diacetate, m.p. 217–218.5° dec. (reported 215–216°,[14] 219–221°[13]); $[\alpha]^{26}\text{D}$ +26.8° (c 1.22, chloroform) (reported $[\alpha]^{18}\text{D}$ +26.6°,[13] $[\alpha]^{9}\text{D}$ +31.5°[14]).

Anal. Calcd. for $C_{20}H_{21}NO_6$: C, 64.68; H, 5.70; N, 3.77. Found: C, 64.51; H, 5.58; N, 3.72.

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[12] The respective melting points of the hydrochloride and picrate of tazettine are reported to be 192 and 214° in *C. A.*, **26**, 4818 (1932) and 214 and 192° in *Chem. Zentr.*, **103**, II, 877 (1932). Recourse to an original copy of reference 1 indicates that the values reported by *C. A.* are in error.

[13] A. Hunger and T. Reichstein, *Helv. Chim. Acta*, **36**, 824 (1953).

[14] H. Kondo and K. Tomimura, *J. Pharm. Soc. Japan*, **48**, 36 (1928).

[15] K. Gorter, *Bull. Jard. Bot. Buitenzorg*, [3] **2**, 1 (1920).

[16] The melting point of this sample of lycorine, when observed in an evacuated capillary, was 282–282.5° dec. This variation in melting point under different conditions has not been reported previously; indeed, reference 13 records the melting point of lycorine on a Kofler block.

[17] A. J. Ewins, *J. Chem. Soc.*, **97**, 2406 (1910).

[18] Y. Asahina and Y. Sugii, *Arch. Pharm.*, **251**, 357 (1913).

Observations on the Forms of Allose and Its Phenylosazone

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In another investigation,[4] a crystalline product was identified as a mixture of DL-allose and D-allose. To attain this objective, it was necessary to establish the nature of the crystalline phases exhibited by this rare hexose and its phenylosazone. β-D-Allose[5]

TABLE I

X-RAY POWDER DIFFRACTION PATTERNS OF THE DIMORPHOUS AND RACEMIC FORMS OF ALLOSE AND ITS PHENYLOSAZONE

β-D- (or β-L)- Allose, m.p. 128°		β-D- (or β-L)- Allose, m.p. 141°		DL- Allose, m.p. 180°		D-(or L)- *ribo*-Hexose phenyl- osazone[a]		DL-*ribo*- Hexose phenyl- osazone[a]	
4.02[b]	(1)[c]	4.26[b]	(1)[c]	4.31[b]	(1)[c]	4.89[b]	(1)[c]	4.66[b]	(1)[c]
4.60	(2)	2.90	(2)	5.94	(2)	3.22	(2)	5.72	(2)
4.21	(3)	5.96	(3)	2.87	(3)	7.68	(3)	4.23	(3)
3.61	(4)	2.69	(4)	3.75	(4)	4.42	(4)	3.16	(4)
2.40	(5)	2.36	(5)	2.32	(5)	3.88	(5)	3.76	(5)
3.14	(6)	2.46	(5)	2.51	(6)	10.26	(6)	4.42	(5)
5.43	(6)	3.67	(6)	5.88	(6)	4.04	(7)	8.82	(6)
7.18	(6)	6.39	(6)	3.94	(7)	2.44	(8)	3.27	(7)
2.89	(7)	1.92	(7)	6.35	(7)	2.84	(8)	10.13	(7)
2.00	(8)	2.01	(7)	1.92	(8)	5.22	(8)	2.00	(8)
2.72	(8)	3.11	(7)	2.10	(8)	3.58	(9)	2.45	(8)
14.09	(8)	3.22	(7)	2.22	(8)	6.51	(10)	2.84	(8)
						6.91	(10)	3.63	(9)
						8.72	(11)	7.76	(10)

[a] The osazones were freshly recrystallized; the racemic form melted at 177–180° dec. and the optically active forms at 162–163° dec. [b] Main interplanar spacings, CuK$_\alpha$ radiation. [c] Relative intensity, estimated visually; 1, strongest band.

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[4] M. L. Wolfrom and J. N. Schumacher, *Science*, **119**, 587 (1954).

[5] F. P. Phelps and F. Bates, THIS JOURNAL, **56**, 1250 (1934).

and β-L-allose,[6] as originally crystallized, were reported to melt, respectively, at 128–128.5° and 128–129°. Both of these sugars have now been found to exist in interconvertible dimorphous forms of m.p. 128° and m.p. 141°. The X-ray powder diffraction patterns of these crystalline phases are shown in Table I. DL-Allose was synthesized from its components and was found to crystallize as fine needles of m.p. 180°. The X-ray powder diffraction pattern exhibited by these crystals (Table I) was different from that of either of the dimorphs of β-D- (or β-L)-allose. Therefore the substance is a true racemic compound.

The crystalline D-,[7–10] L-[6,10] and DL-[10] forms of *ribo*-hexose phenylosazone[11] (*synonyms* allose, altrose, psicose, allulose phenylosazone) were freshly prepared and their X-ray powder diffraction patterns were ascertained (Table I). The racemic form again gives a pattern different from that of either component and is therefore a true compound. Good patterns are exhibited only by the freshly crystallized osazones and this fact may be used as further evidence that the phenylosazones can no longer be considered as derivatives of choice for the sugars. Clark and co-workers[12] report an X-ray powder diffraction pattern for a substance purported to be D-*ribo*-hexose phenylosazone.[11] Their data do not agree exactly with those which we record for either the DL or D form.

Experimental

Dimorphism of β-D-Allose and β-L-Allose.—A sample of β-D-allose, m.p. 128°, was found to have changed in melting point to 141° on storage. Its direction of mutarotation was unchanged. A sample of β-L-allose which had been stored for many years was found to still melt at 128° and its X-ray powder diffraction lines (Table I) were different from those of the higher melting form of β-D-allose. When the β-L-allose (m.p. 128°) was placed near a recently prepared sample of L-allose, it was converted to the higher melting (141°) form and the X-ray powder diffraction lines were then identical with those of β-D-allose (m.p. 141°). Recrystallization of the β-L-allose (m.p. 141°) from water–ethanol lowered the melting point to 130–131° and this preparation exhibited the X-ray powder diffraction lines characteristic of the lower melting form.

DL-Allose.—Accurately weighed equal amounts of the dimorphs (m.p. 141°) of β-D-allose and β-L-allose were recrystallized from water–ethanol; m.p. 180°, fine needles, X-ray powder diffraction lines recorded in Table I. The substance is a racemic compound.

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The Condensation of Chloropyruvic Acid with Chlorobenzene

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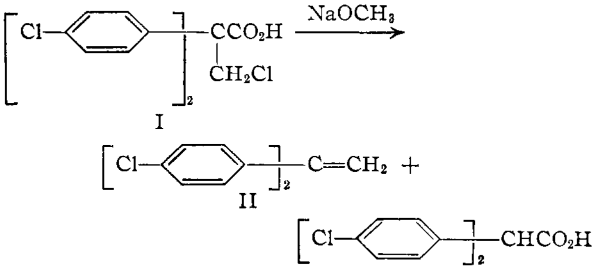
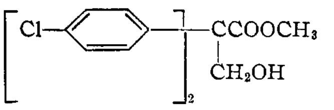
The sulfuric acid induced condensation of bromo- and chloropyruvic acids with benzene has been reported.[1,2] In this note the reaction of chloropyruvic acid with chlorobenzene to give a 33% yield of 2,2-di-(*p*-chlorophenyl)-3-chloropropanoic acid (I) is described. The *para* orientation of the halogen atoms was established by the fact that refluxing I with sodium methoxide in methanol followed by alkaline hydrolysis produced a mixture of the two known compounds, 1,1-di-(*p*-chlorophenyl)-ethylene (II) and di-(*p*-chlorophenyl)-acetic acid (III).



The formation of ethylenes of type II from anions of β-halocarboxylic acids is well known. The acid III, however, must be formed as a secondary degradation product of an intermediate β-lactone, which reacts under the experimental conditions to give the β-hydroxy ester IV. In the presence of



IV

sodium methoxide this ester then suffers a reverse aldol cleavage to form the methyl ester of III.[3] Attempts to prepare the β-lactone by treatment of I with an equivalent amount of aqueous sodium hydroxide failed to produce an isolable product. In contrast, the unsubstituted 2,2-diphenyl-3-chloropropanoic acid gives almost a quantitative yield of the corresponding β-lactone under identical conditions.[4]

The acid I was only weakly insecticidal.

Acknowledgment.—The authors are indebted to Mr. E. F. Shelberg for the microanalyses.

Experimental

2,2-Di-(*p*-chlorophenyl)-3-chloropropanoic Acid (I).—To a suspension of 57 g. (0.46 mole) of chloropyruvic acid[5] in 450 cc. of concentrated sulfuric acid was added dropwise with stirring at room temperature 207 g. (1.84 moles) of chlorobenzene. After stirring at room temperature for 20 hours, the red solution was poured into ice, the precipitated oil was taken up in ether, washed well with water and dried over anhydrous magnesium sulfate. Filtration, removal of the ether by distillation, trituration of the residue with heptane and crystallation of the crude solid from an ether–pentane mixture gave 50 g. (33%) of condensation product I, m.p. 155–157°. Three more recrystallizations of a sample for analysis gave product of m.p. 157–158°.

Anal. Calcd. for $C_{15}H_{11}Cl_3O_2$: C, 54.65; H, 3.36. Found: C, 54.78; H, 3.28.

Treatment of 2,2-Di-(*p*-chlorophenyl)-3-chloropropanoic Acid (I) with Sodium Methoxide in Methanol.—To a solution of sodium methoxide prepared from 0.46 g. (0.02 gram-atom) of sodium in 60 cc. of dry methanol was added 3.3 g.

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