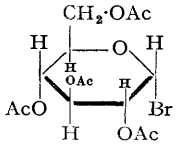
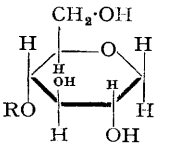
NOTES.

41. *Catalytic Reduction of Acetobromo-sugars.*

By L. ZERVAS and MISS C. ZIOUDROU.

FISCHER and ZACH (*Sitzungsber. kgl. preuss. Akad. Wiss.*, 1913, **16**, 311; *Chem. Zentr.*, 1913, I, 1668) attempted to synthesise an anhydrohexitol by the zinc dust reduction of tetra-*O*-acetyl-α-D-glucosyl bromide (I), but obtained glucal instead. We have found that the anhydrohexitol is obtained by catalytic hydrogenation with palladium as catalyst, in the presence of a tertiary base such as triethylamine or 4-ethylmorpholine. After removal of the acetyl groups, polygalitol (II*a*) was obtained, identical with that from various *Polygala* species (Piccard, *Bull. Soc. Chim. biol.*, 1927, **9**, 692; Shinoda, Sato, and Sato, *Ber.*, 1932, **65**, 1219; Freudenberg and Rogers, *J. Amer. Chem. Soc.*, 1937, **59**, 1602). The previous (Richtmyer, Carr, and Hudson, *J. Amer. Chem. Soc.*, 1943, **65**, 1477) and this new synthesis further support the formulation of polygalitol as 1 : 5-anhydro-D-sorbitol (Freudenberg and Rogers, *loc. cit.*; Richtmyer and Hudson, *J. Amer. Chem. Soc.*, 1943, **65**, 64).

(I) 



(II) *a* : R = H
b : R = $C_6H_{11}O_5$

The tertiary base could hydrolyse the tetra-*O*-acetylglucosyl bromide to tetra-*O*-acetylglucose, form a trialkylglycosylammonium salt, or eliminate hydrogen bromide to form tetra-*O*-acetyl-2-hydroxyglucal. If the last compound had been formed in large amount,

the main product of the catalytic reduction would have been styracitol, 1 : 5-anhydro-D-mannitol (Zervas, *Ber.*, 1930, **63**, 1689). Therefore, in order to slow down the rates of the above side reactions, the reduction was carried out in dilute anhydrous solution containing the theoretical amount of tertiary base and with a relatively large amount of catalyst.

Other acetobromo-sugars can also be reduced by this procedure. Thus, hepta-*O*-acetylcellobiosyl bromide gave finally 1 : 5-anhydro-4-(β-D-glucopyranosyl)-D-sorbitol (II*b*).

Experimental.—1 : 5-*Anhydro*-D-*sorbitol* (polygalitol). To the solution of 4·1 g. (0·01 mole) 2 : 3 : 4 : 6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (4·1 g., 0·01 mole) in anhydrous ethyl acetate (80 ml.), triethylamine (1 g., 0·01 mole) was added and the mixture was immediately hydrogenated in the presence of 0·5 g. of freshly prepared palladium black. Depending on the catalyst activity the hydrogenation was complete in 60—90 min., when 250 ml. of hydrogen had been absorbed (26°/756 mm.). The filtrate was twice washed with water and evaporated to dryness *in vacuo*. The syrupy residue, mainly consisting of polygalitol tetra-acetate mixed with a small quantity of tetra-acetylglucosyl bromide and other products, was treated with N-alcoholic potassium hydroxide (50 ml.) for 4 hr. at room temperature. Then, 2N-sulphuric acid (25 ml.) was added and the mixture was evaporated to dryness *in vacuo*. The residue was repeatedly extracted with absolute methanol and the combined filtrates were evaporated to dryness *in vacuo*. Complete removal of the inorganic salts was ensured by dissolving the residue in absolute methanol and concentrating the filtered solution to a few ml. At 0°, 0·65 g. (40%) of polygalitol separated, having m. p. 142—143°, $[\alpha]_D^{20}$ +42·1° (*c* 1·5 in H_2O) (Found : C, 43·75; H, 7·1. Calc. for $C_6H_{12}O_5$: C, 43·9; H, 7·4%). Freudenberg and Rogers (*loc. cit.*) gave m. p. 142—143°, $[\alpha]_D$ +42·8—45°; Richtmyer, Carr, and Hudson (*loc. cit.*) gave m. p. 140—141°, $[\alpha]_D$ +42·4°.

Acetylation with acetic anhydride–pyridine gave polygalitol tetra-acetate, m. p. 75°, in almost quantitative yield (Richtmyer, Carr, and Hudson, *loc. cit.*, gave m. p. 73—74°).

1 : 5-*Anhydro*-4-(β-D-*glucopyranosyl*)-D-*sorbitol*.—Hepta-*O*-acetylcellobiosyl bromide (7 g., 0·01 mole) in ethyl acetate in the presence of triethylamine (1 g.) was catalytically hydrogenated as described above. Evaporation of the filtrate to dryness and recrystallisation of the residue from ethanol gave hepta-*O*-acetyl-1 : 5-anhydro-4-(β-D-glucopyranosyl)-D-sorbitol (4·5 g., 72%) as needles, m. p. 194°, $[\alpha]_D^{25}$ +4·6° (*c*, 10 in $CHCl_3$) (Fletcher and Hudson, *J. Amer. Chem. Soc.*, 1948, **70**, 310, gave m. p. 194—195°, $[\alpha]_D$ +4°).

Hydrolysis by Fletcher and Hudson's procedure (*loc. cit.*) afforded 1 : 5-anhydro-4-(β-D-glucopyranosyl)-D-sorbitol (85%), m. p. 172°, $[\alpha]_D^{25}$ +29·5° (*c* 4 in H_2O) (Found : C, 44·3; H, 6·9. Calc. for $C_{12}H_{22}O_{10}$: C, 44·3; H, 6·8%). Fletcher and Hudson (*loc. cit.*) and Maurer and Ploetner (*Ber.*, 1931, **64**, 281) gave m. p. 172°, 173°, $[\alpha]_D$ +29°, 29·3° (in H_2O).

This investigation was supported by a grant from the Rockefeller Foundation whom we thank.

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42. Rauwolfia *Alkaloids. Part I. Reserpine and Ajmaline from* Rauwolfia natalensis *Sond.* (R. caffra).

By BRUNO O. G. SCHULER and F. L. WARREN.

Rauwolfia natalensis Sond. (*R. caffra*), which is locally known as the quinine tree, is used medically by the Bantu. The Zulus use extracts for skin rashes, and the Pondos employ the bark for intestinal disorders.

Juritz (*Report Sen. Analyst, Cape Good Hope*, 1901, 58) reported the isolation of a bitter alkaloid, m. p. 200°, from a plant which he finally characterised as *R. natalensis* (*S. African J. Sci.*, 1914, **11**, 110). Rindl and Groenewoud (*Proc. Roy. Soc. S. Africa*, 1932, **21**, 55) re-investigated *R. caffra* but isolated only amorphous alkaloidal material, one portion of which gave a perchlorate as needles (not analysed), m. p. 110—113°.

In view of the interest in this species we have re-investigated *R. caffra*. The aerial bark gave only small quantities of alkaloid which was intractable. Extraction of the root

bark in the cold by the elegant method of Djerassi, Gorman, Nussbaum, and Reynoso (*J. Amer. Chem. Soc.*, 1954, **76**, 4463) gave reserpine, m. p. 262—263°, in small quantities. The main alkaloid, m. p. 158—161°, was identified as ajmaline by its colour reactions with ferric chloride and nitric acid (cf. Anet, Chakravarti, Robinson, and Schlittler, *J.*, 1954, 1246), and by the comparison of its properties and those of its derivatives with those reported by Siddiqui and Siddiqui (*J. Indian Chem. Soc.*, 1931, **8**, 667; 1932, **9**, 539; 1955, **12**, 37) and by Anet *et al.* (*loc. cit.*). This comparison is shown in the Table.

Isolated alkaloid compared with ajmaline.

	Anet *et al.*	Siddiqui	This paper
Ajmaline	158—160°	158—160°	158—161°
$[\alpha]_D$	+144 (anhyd.)	+128 (hydr.)	+128 (hydr.)
Hydrochloride (hydr.)	250 (cryst.)	253—255 (amorphous)	254 (cryst.)
Picrate (hydr.)	—	126—127	125
Picrate (anhyd.)	—	223	220
Oxime HCl	218	—	214—218

This alkaloid showed ultraviolet maxima at 250 and 292 mμ (log ε 3·95 and 3·55 respectively) and infrared bands at 3·00, 3·17, 3·5—4·00, and 6·21 μ. Absorption in these regions has been reported for ajmaline by Anet *et al.* (*loc. cit.*). In carbon tetrachloride absorption was also observed at 5·83 μ indicative of a carbonyl group as reported by Chatterjee and Bose (*Experientia*, 1953, **9**, 254): in agreement, however, with the observations by Anet *et al.* (*loc. cit.*) we were unable to detect this band when the spectrum was measured in Nujol or chloroform. This band is broad and weak as might be expected from a dynamic carbinol–amine system envisaged in the Robinson–Schlittler (*loc. cit.*) formula.

The infrared spectrum in the skeletal region was identical with that of a specimen kindly supplied by Dr. E. Schlittler of Ciba Pharmaceutical Products Inc. In spite of the difference in infrared spectrum in the different solvents, the spectra of ajmaline hydrochloride and of the freshly regenerated base were identical in the ultraviolet so that the ready isomerism observed by Skinner (*J.*, 1950, 823) for cotarnine and berberine does not exist.

Experimental.—Extraction. A mixture of ether (1·7 l.), benzene (500 ml.), and ethanol (200 ml.) was added to finely ground root bark (200 g.) of *R. caffra*, collected in March in the Pietermaritzburg district of Natal. After 15 min. 7N-ammonia (400 ml.) was added, the whole shaken for 2 days under nitrogen, and the solution filtered. The residue was extracted twice more by the same procedure. The combined extracts were evaporated at <35° under reduced pressure. The dry residue was extracted with benzene (2 × 100 ml.), and the benzene solution run through a column of alumina (75 g.; activity II). The benzene eluates gave a non-alkaloidal amorphous powder, m. p. 139°. Ether gave a gum, a methanol solution of which on evaporation gave rod-like crystals which were removed. The mother-liquor slowly deposited crystalline nodules.

The nodules, crystallised from methanol, gave reserpine (30 mg.), m. p. 262—263°, undepressed by specimen kindly supplied by Parke Davis, Detroit (Found: N, 4·5. Calc. for $C_{33}H_{40}O_9N_2$: N, 4·6%). Muller, Schlittler, and Bein (*Experientia*, 1952, **8**, 338) give m. p. 262—263°. The infrared spectra of the two samples were identical.

The rod-shaped crystals, crystallised from methanol, gave ajmaline as rectangular plates (1 g.), m. p. 158—161°, with previous swelling at 142° (Found: C, 70·4; H, 8·6; N, 7·8. Calc. for $C_{20}H_{26}O_2N_2,CH_4O$: C, 70·4; H, 8·4; N, 7·8%). Ajmaline hydrochloride, dried at 100° for 3 hr., had m. p. 254° (Found: C, 59·9; H, 7·3. Calc. for $C_{20}H_{26}O_2N_2,2HCl$: C, 60·1; H, 6·9%).

The authors acknowledge with thanks grants from the S.A.C.S.I.R. and the interest shown by Dr. W. S. Rapson, Director of the N.C.R.L., in these studies.

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University of Natal, Pietermaritzburg, S. Africa. [*Received, July 26th*, 1955.]

43. *The Melting Point and Magnetic Susceptibility of Zinc Chloride.*

By D. A. Craw and J. L. Rogers.

During an investigation of thermodynamic properties of the copper–zinc system, pure anhydrous zinc chloride was required for use in alloy concentration cells. Published m. p.s of zinc chloride ranged from 239° (Lorenz and Michael, *Z. phys. Chem.*, 1928, **137**, *A*, 1) to 365° (Grünauer, *Z. anorg. Chem.*, 1904, **39**, *A*, 389); handbooks and textbooks generally quote figures between 262° and 290°. A reliable determination of the melting point was therefore necessary.

Experimental.—Dry hydrogen chloride was passed over pure mossy zinc at 410° and the slowly formed molten zinc chloride collected out of contact with the air in m. p. tubes. Initially the brass-block method was used to determine the m. p. as 318°, in close agreement with the reports by Biltz and Klemm (315° ± 3°; *Z. phys. Chem.*, 1924, **110**, 333) and of Klemm (318° ± 2°; *Z. anorg. Chem.*, 1926, **152**, 235).

The chloride was also prepared by a method due to Biltz and Klemm (*loc. cit.*) and Grünauer (*loc. cit.*), who, however, reported a considerably different m. p. Dry hydrogen chloride was passed through crystalline zinc chloride (" Anachemia " reagent grade) for 10 min., then the zinc chloride was heated slowly past its m. p. and dry hydrogen chloride was continuously bubbled through the melt at 350° for a further 45 min. Purified dry argon was exchanged for the hydrogen chloride gas and passed for 20 min. before the zinc chloride was transferred out of contact with the air to m. p. tubes. This method of dehydration was repeated several times with minor variations and a constant m. p. 318° ± 2° found (Found: Zn, 47·8; Cl, 52·0. Calc. for $ZnCl_2$: Zn, 48·0; Cl, 52·05%).

The m. p. for the latter preparation was determined in an apparatus similar to that described by White (*Analyt. Chem.*, 1947, **19**, 432). Hartwell (*ibid.*, 1948, **20**, 374), in an investigation of melting-bath liquids, recommended the use of a Silicone oil (General Electric 9981-LTNV-40) for the 300° region and this proved entirely satisfactory. Stem correction was made for the mercury-in-glass thermometer whose accuracy was checked by comparison with a Pt–Pt-13%Rh thermocouple previously calibrated at the f. p. of tin, lead, and zinc.

No workers have reproduced the m. p. obtained by Grünauer (365°); he gave no analysis of his product or temperature calibration, and it seems certain that this work was in error.

The magnetic susceptibility of zinc chloride (but not that of carefully dehydrated zinc chloride) has been measured previously, either with crystalline zinc chloride (Flordal and Frivold, *Ann. Physik*, 1935, **23**, 425) or in aqueous solution (Kido, *Sci. Reports Tokoku Univ.*, Ser. 1, 1932, **21**, 149; König, *Ann. Physik Chem.*, 1887, **31**, 273). The magnetic susceptibility of anhydrous zinc chloride was measured by one of us (J. L. R.) by a modified Gouy method (Henry and Rogers, to be published) and, the determined density of 2·79 ± 0·05 g./c.c. at 23° being used, the mass susceptibility was calculated as $-0{\cdot}47_7 \times 10^{-6} \pm 0{\cdot}010 \times 10^{-6}$ e.m.u. at 23°. If Flordal and Frivold's figure (*loc. cit.*) for the susceptibility of crystalline zinc chloride is corrected for the use of a different standard, it becomes $-0{\cdot}458 \times 10^{-6}$ e.m.u.

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44. 3- *and* 5-*Ethyloctahydropyrrocolines.*

By K. S. N. Prasad and R. Raper.

Clemo [1] obtained, by the alkaline degradation of strychnine, a bicyclic base whose octahydro-derivative has the composition of an ethyl- or dimethyl-octahydropyrrocoline. Various bases of this type have been synthesised,[2] all of which differed from the reduced strychnine derivative. We have now synthesised 3- and 5-ethyloctahydropyrrocoline (I) and (II), neither of which is identical with the reduced base from the alkaloid.

Ethyl 2-piperidylacetate was condensed with ethyl α-bromobutyrate, and the product

[1] Clemo, *J.*, 1936, 1695.
[2] Clemo, Fox, and Raper, *J.*, 1953, 4173.

cyclised to a ketone which on reduction gave the 3-ethyl compound (I). 2 : 6-Lutidine was converted by means of formaldehyde into the alcohol. Dehydration and reduction of the resulting vinyl derivative gave 2-ethyl-6-methylpyridine which was converted into ethyl 6-ethyl-2-pyridylacetate by the usual method. This ester differed from the isomer,

(I)   (II)

ethyl α-(6-methyl-2-pyridyl)propionate, made by methylation of the corresponding acetate. Hydrogenation of the 6-ethyl acetate, condensation of the resulting piperidine with ethyl bromoacetate, cyclisation, and reduction gave the 5-ethyl-pyrrocoline (II).

Experimental.—Ethyl α-2-(ethoxycarbonylmethyl)piperidinobutyrate. Ethyl 2-piperidylacetate [3] (5 g.), ethyl α-bromobutyrate (6·5 g.), and anhydrous potassium carbonate (5 g.) were heated at 100° with occasional stirring for 10 hr. Water was added and the oil taken up in ether, dried, and distilled. The *ester* (5 g.) had b. p. 140—145°/2 mm. (Found : C, 63·6; H, 9·7. $C_{15}H_{27}O_4N$ requires C, 63·2; H, 9·5%).

3-Ethyloctahydro-2-oxopyrrocoline.—The above diester (3 g.) in dry toluene (5 ml.) was added to powdered potassium (1 g.), suspended in toluene (5 ml.) cooled in ice. After the vigorous reaction was over the mixture was heated for 4 hr. (water-bath), alcohol was added to dissolve unchanged metal, followed by water (15 ml.) and concentrated hydrochloric acid (20 ml.). The solution was heated for 20 hr. (water-bath) and evaporated to dryness in a vacuum. The residue was basified (50% potassium hydroxide), and the *ketone* extracted with ether, dried, and distilled (1 g.; b. p. 120—125°/12 mm.) (Found : C, 71·7; H, 10·5. $C_{10}H_{17}ON$ requires C, 71·8; H, 10·2%). The *picrate*, from ethanol, has m. p. 165° (Found : C, 48·5; H, 5·5. $C_{10}H_{17}ON,C_6H_3O_7N_3$ requires C, 48·5; H, 5·1%).

3-Ethyloctahydropyrrocoline.—The ketone (0·8 g.), amalgamated zinc (5 g.), and concentrated hydrochloric acid (12 ml.), were set aside for 2 hr. and then refluxed for 24 hr. The decanted liquid was strongly basified (50% potassium hydroxide) and the *base* extracted with ether, dried, and distilled [0·35 g.; b. p. (bath temp.) 140—150°/12 mm.] (Found : N, 8·8. $C_{10}H_{19}N$ requires N, 9·1%). The *picrolonate*, from ethanol, has m. p. 140° (Found : C, 57·7; H, 6·8. $C_{10}H_{19}N,C_{10}H_8O_5N_4$ requires C, 57·5; H, 6·5%).

2-2′-Hydroxyethyl-6-methylpyridine. 2 : 6-Lutidine (64 g.) was converted into its lithium derivative [4] the ethereal solution of which was cooled in a freezing mixture, and formaldehyde from paraformaldehyde (40 g.) passed into it. After being stirred for 45 min. and refluxed for a similar period the product was decomposed with ice and hydrochloric acid, the ether layer removed, the aqueous layer basified (potassium hydroxide), and the *base* extracted with chloroform, dried (K_2CO_3), and distilled (25 g.; b. p. 120—125°/12 mm.) (Found : C, 69·85; H, 8·3. $C_8H_{11}ON$ requires C, 70·1; H, 8·0%). Its *picrate*, from ethanol–ether, has m. p. 97° (Found : C, 45·4; H, 3·8. $C_8H_{11}ON,C_6H_3O_7N_3$ requires C, 45·9; H, 3·8%). 2 : 6-Lutidine (20 g.) was recovered.

2-Methyl-6-vinylpyridine. The above alcohol (25 g.) was dehydrated with potassium hydroxide (10 g.) for 6 hr. at 100°/12 mm., the crude product distilling off. It was dried in ethereal solution (Na_2SO_4) and formed an *oil* (19 g.; b. p. 65—70°/12 mm.) (Found : C, 81·2; H, 7·9. C_8H_9N requires C, 80·7; H, 7·6%). Its *picrate*, from ethanol, has m. p. 163° (Found : C, 47·9; H, 3·7. $C_8H_9N,C_6H_3O_7N_3$ requires C, 48·2; H, 3·4%).

2-Ethyl-6-methylpyridine. The vinylpyridine (18 g.) was hydrogenated in ethanol (50 ml.), over palladised charcoal (3 g.; 5%) at 20° and atmospheric pressure, giving the *ethylpyridine* (16 g.; b. p. 68—73°/12 mm.) (Found : C, 79·5; H, 9·3. $C_8H_{11}N$ requires C, 79·3; H, 9·1%). The *picrate*, from ethanol, has m. p. 125° (Found : C, 48·0; H, 4·3. $C_8H_{11}N,C_6H_3O_7N_3$ requires C, 48·0; H, 4·0%).

Ethyl 6-ethyl-2-pyridylacetate. This was prepared from the above base (15 g.) by Woodward and Kornfeld's method.[4] Unchanged base (4 g.) and the *ester*, a pale yellow oil (7 g.; b. p. 134—137°/12 mm.), were obtained (Found : N, 7·6. $C_{11}H_{15}O_2N$ requires N, 7·3%). The *picrolonate*, from ethanol, has m. p. 157° (Found : C, 54·6; H, 5·0. $C_{11}H_{15}O_2N,C_{10}H_8O_5N_4$ requires C, 55·1; H, 5·0%).

[3] Clemo, Morgan, and Raper, *J.*, 1935, 1743.
[4] Woodward and Kornfeld, *Org. Synth.*, 1949, **29**, 44.

Ethyl 6-ethyl-2-piperidylacetate. This was obtained by hydrogenating the above ester (7 g.) in glacial acetic acid (30 ml.) over platinum oxide (0·1 g.) for 24 hr. at room temp. and 100 lb./sq. in. pressure, adding more catalyst (0·1 g.), and shaking the mixture a further 24 hr. The *ester* (6·5 g.) had b. p. 116—120°/12 mm. (Found: C, 65·8; H, 10·6. $C_{11}H_{21}O_2N$ requires C, 66·3; H, 10·6%).

Diethyl 6-ethylpiperidine-1 : 2-diacetate. Ethyl 6-ethyl-2-piperidylacetate (6 g.) and ethyl bromoacetate (6 g.) reacted, in presence of anhydrous potassium carbonate (as above), to give the *diacetate* (4·8 g.; b. p. 138—143°/2 mm.) (Found: C, 62·9; H, 9·7%).

5-Ethyloctahydro-2-oxopyrrocoline. The diacetate (3 g.), cyclised with the aid of potassium, and decarboxylated as described above, gave the *ketone* (1 g.; b. p. 118—123°/12 mm.) (Found: C, 71·3; H, 10·5%). The *picrate*, from ethyl acetate, has m. p. 158° (decomp.) (Found: C, 48·6; H, 5·3%).

5-Ethyloctahydropyrrocoline. When the 2-keto-derivative (0·5 g.) was reduced (Clemmensen) *5-ethyloctahydropyrrocoline* [0·2 g.; b. p. 140—150° (bath temp.)] was obtained (Found: N, 8·9%). The *picrate*, from ethanol, has m. p. 175° (Found: C, 50·2; H, 5·7. $C_{10}H_{19}N,C_6H_3O_7N_3$ requires C, 50·3; H, 5·8%).

Ethyl α-(6-methyl-2-pyridyl)propionate. Ethyl 6-methyl-2-pyridylacetate [5] (5·5 g.) was treated with powdered potassium (1·2 g.) in ether (60 ml.). Methyl iodide (4·4 g.) was carefully added to the potassium derivative, and the whole refluxed 10 hr. Water (20 ml.) was added, and the *ester* extracted with ether, dried, and distilled (3·6 g.; b. p. 120—123°/4 mm.) (Found: N, 7·5%). The picrolonate, from alcohol, has m. p. 170° (Found: C, 55·0; H, 5·2%).

KING'S COLLEGE, NEWCASTLE UPON TYNE, 1. [*Received, July 29th*, 1955.]

[5] Clemo, Fox, and Raper, *J.*, 1954, 2693.

45. *Crystalline* 2 : 3-*Di*-O-*methyl*-β-D-*xylose.*

By ERIC G. MEEK.

SYRUPY 2 : 3-di-*O*-methyl-D-xylose was first isolated from the hydrolysate of methylated esparto xylan by Hampton, Haworth, and Hirst (*J.*, 1929, 1739). Chanda, Hirst, Jones, and Percival (*J.*, 1950, 1289) also obtained it from the same source; after two years their specimen crystallised in the α-form, and had m. p. 79—80°, $[\alpha]_D^{15}$ +70° (3 min.), +23° (14 hr., constant) (*c* 1·0 in H_2O) (Chanda, Percival, and Percival, *J.*, 1952, 260). Hirst, Percival, and Wylam (*J.*, 1954, 189), and Aspinall and Mohamed (*J.*, 1954, 1731), have also isolated this ether in the α-form.

The β-isomer of 2 : 3-di-*O*-methyl-D-xylose has now been obtained despite the fact that the syrupy ether was seeded with Chanda, Percival, and Percival's α-crystals.

The α- and the β-isomer have the same m. p., but this was depressed on admixture: they gave different *X*-ray powder photographs and different infrared spectra. All attempts to obtain more α-crystals have been unsuccessful; syrups left unseeded, or seeded with α- or β-crystals have either remained syrupy or given β-crystals.

Experimental.—All rotations were measured in 1 dm. tubes. Zero time was taken to be the time of addition of the solvent: dissolution was usually complete in 3—5 min.

Hydrolysis of a methylated wheat-straw xylan, and cellulose column chromatography yielded syrupy 2 : 3-di-*O*-methyl-D-xylose which was characterised as its aniline derivative and as 2 : 3-di-*O*-methyl-D-xylonamide. The syrup was seeded with Chanda, Percival, and Percival's α-crystals; crystallisation was almost complete in two weeks. After draining on porous tile to remove traces of syrup the β-*form* had m. p. 79—80° (mixed m. p. with Chanda, Percival, and Percival's sample 65—67°), $[\alpha]_D^{20}$ −7·3° (5 min.), +4·4° (10 min.), +13·8° (15 min.), +24·2° (25 min.), +26·7° (35 min., constant) (*c* 2·0 in H_2O); $[\alpha]_D^{20}$ −30·3° (10 min.), −23·0° (30 min.), −9·9° (70 min.), −0·5° (110 min.), +9·9° (190 min.), +14·9° (280 min.), +18·1° (380 min., constant) [*c* 2·2 in EtOH–H_2O (4 : 1)] (Found: C, 46·7; H, 7·8; OMe, 34·6. $C_7H_{14}O_5$ requires C, 47·2; H, 7·9; OMe, 34·8%).

Chanda, Percival, and Percival's crystals had $[\alpha]_D^{19}$ +40·6° (10 min.), +36·0° (30 min.), +29·0° (75 min.), +24·6° (115 min.), +17·4° (220 min.), +14·5° (320 min.), +12·6° (585 min., constant) [*c* 2·1 in EtOH–H_2O (4 : 1)].

In view of the very rapid initial changes in rotation, even in aqueous ethanol, Hudson's rule could not be applied with accuracy.

Dr. S. A. Barker of Birmingham University kindly examined these samples and reported: " Both specimens showed very similar spectra over a wide range with only slight changes in wave number. However, the most striking difference was that the α-form had two peaks, at 1230 and 736 cm.$^{-1}$, not present in the β-form. The latter is due to symmetrical ring breathing frequency and has been found in all other derivatives of xylose in the α-form, but never in the β-form " (cf. Barker, Bourne, Stephens, and Whiffen, *J.*, 1954, 3468).

X-Ray powder photographs were taken by courtesy of Dr. C. A. Beevers with a Raymax tube with a copper target. The heavier lines given by both samples lay in the same region but had different spacings and intensities, thus indicating different crystal structures. The crystalline sample of 2 : 3-di-*O*-methyl-D-xylose obtained by Aspinall and Mohamed (*loc. cit.*) gave a photograph identical with that given by Chanda, Percival, and Percival's α-isomer.

The author thanks Professor E. L. Hirst, F.R.S., Dr. G. O. Aspinall, and Dr. E. Percival for helpful advice, and the British Rayon Research Association for the award of a Fellowship.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, EDINBURGH. [*Received, August 3rd,* 1955.]

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46. *Carbohydrates of the Roots of the Parsnip,* Pastinaca sativa.

By D. M. W. ANDERSON and C. T. GREENWOOD.

DURING the isolation of starch from parsnips, *Pastinaca sativa,* other polysaccharides present in the roots were separated by successive extractions with cold water, hot water, cold 5% sodium hydroxide, and hot 5% sodium hydroxide. Results of analyses of the fractions obtained are shown in the Table.

Analyses of fractions isolated from parsnip roots (% of dry weight).

Fraction	Yield	Ash *	Protein †	Uronic acid anhydride	Polysaccharide ‡	Sugars obtained on hydrolysis §						
						Gal	G	M	A	X	R	F
P1 (cold water sediment)	28	0·4	37·1	8·8	53·7	1·3	46·2	0	4·9	0·8	0·6	0
P2 (,, extract)	20	17·4	24·2	7·4	51·0	11·2	24·4	0	12·8	1·6	0	1·0
P3 (hot water ,,)	13	6·6	6·2	41·5	45·7	6·0	17·6	0	17·0	1·4	3·7	0
P4 (cold NaOH ,,)	14	7·5	13·4	23·4	55·7	13·2	5·1	3·4	26·2	5·6	2·2	0
P5 (hot ,, ,,)	5	7·4	5·5	45·3	40·8	9·2	3·2	2·9	23·4	1·6	0·4	0
P6 (residue) [a]	11	3·1	0	2·2	12·7	0·8	9·1	0	0·9	2·0	0	0

* Not sulphated. † %N × 6·25.

‡ Hydrolysable non-acidic polysaccharide (calculated by difference).

§ Hydrolysis conditions: 2% H_2SO_4 in a sealed tube at 98° for 7 hr.

Chromatographic conditions: butan-1-ol–benzene–pyridine–water (5 : 1 : 3 : 3; top layer) solvent phase; 48 hr. development time; aniline oxalate spray for aldoses; urea oxalate for ketoses; estimations by Somogyi's reagent.

Gal = galactose; G = glucose; M = mannose; A = arabinose; X = xylose; R = rhamnose; F = fructose.

[a] This fraction was only 18% hydrolysed under these conditions (see text).

Examination of the unhydrolysed cold water extract (P2) by chromatography indicated that raffinose, sucrose, glucose, and fructose were present as free sugars, together comprising about 2% of the fraction. No polyfructosans were detected. No free sugars were present in any of the other fractions. Hydrolysis of fractions P1, P3, P4, and P5 liberated a sugar which behaved chromatographically as rhamnose. Rhamnose may, however, be readily confused with D(+)-apiose under these conditions, and the latter has been shown to exist in other members of the *Umbelliferae.*[1] Comparison with authentic D(+)-apiose (kindly placed at our disposal by Dr. D. J. Bell) established that the sugar was in fact rhamnose. The presence of this sugar in plant materials is not unusual.[2] Fraction (P6) was only 18% hydrolysed under the conditions described, but the residue on treatment with 72% sulphuric

[1] Bell, Isherwood, Hardwick, and Cahn, *J.*, 1954, 3702.

[2] Cf. Hirst, *J.*, 1949, 522.

acid gave 95% of glucose together with traces of xylose, and was therefore cellulosic material, (2% of lignin remained).

Traces only of alkali-soluble mannan exist, and surprisingly little xylan is present. The uronic acid content of all fractions is high, however, and the roots provide a good source of pectic material and also of araban. The starch (from P1) in unusual in that potentiometric titrations with iodine have shown it to contain only 11·1% of amylose,[3] and this material is being investigated in detail

Experimental.—Before analysis, samples were dried at 80° *in vacuo* for several hours. Solutions were concentrated under reduced pressure at 40°. Percentages of nitrogen were determined by duplicate semi-micro Kjeldahl determinations, whilst estimations of uronic acid anhydride were made by McCready's method.[4]

Extraction of roots. (*a*) Removal of oil. Parsnips were peeled, minced, and then exhaustively extracted by successive treatments with boiling methanol, methanol–benzene (2 : 1 v/v), and ether (Found, on defatted material: ash, 3·02; protein, 16·2; uronic acid anhydride, 22·4%).

(*b*) Extractions with water. Defatted roots (55 g.) were extracted with cold water (8 × 300 ml.; each 3 min.) in an " Atomix " blender. Each extract was filtered through muslin to yield on centrifugation a protein-contaminated starch (P1) and supernatant liquors. The latter when reduced in valume and freeze-dried yielded the cold-water extract (P2). The residual material was similarly extracted with water at 98°, and the polysaccharides isolated by freeze-drying to yield fraction (P3).

(*c*) Extractions with alkali. The residue was vigorously stirred with 5% sodium hydroxide (w/v : 8 × 200 ml.; each 1 hr.) at room temperature, and then at 98°. In each case the alkaline extract after centrifugation was brought to pH7 with acetic acid. The volume was then reduced, salts were removed by dialysis for 96 hr., and the fractions (P4 and P5, respectively) were isolated by freeze-drying. The final residue was washed free from alkali and dried (P6).

The overall yield was 91% of the dry weight of original material.

Analysis of fractions. Qualitative and quantitative estimations of the sugars liberated on hydrolysis were carried out as previously described,[5] with the exception that separation of arabinose from mannose in fractions P4 and P5 was achieved by use of ethyl acetate–acetic acid–water (3 : 1 : 3 v/v; non-aqueous phase) as solvent.[6]

With the exception of fructose (which is about 35% decomposed), the liberated sugars were stable under the hydrolysis conditions used (see Wylam [8]). (Since fructosans were absent, the appearance of fructose in hydrolysed P2 was only supplementary to the results obtained from a study of the unhydrolysed cold-water extract.) A weighed amount of ribose was added to each fraction (preliminary experiments having shown this sugar to be absent from all hydrolysates) to permit estimation of losses during analysis. In each case, the total weight of sugars found was between 75 and 90% of the expected quantities. Values quoted in the table have been corrected, the loss for each sugar being assumed to be proportionate to the actual weight found.

Although uronic acids were present in all hydrolysates (naphtharesorcinol test), no attempt was made to separate them chromatographically.

Confirmation of the presence of rhamnose. The acid hydrolysates of fractions P1, P3, P4, and P5 were examined chromatographically without preliminary neutralization,[7] since apiose is extremely reactive to alkali.[1] The R_F value (0·24) of the suspected rhamnose and of an authentic sample of rhamnose was the same when duplicate chromatograms were run with (*a*) butan-1-ol saturated with water, and (*b*) butan-1-ol saturated with aqueous boric acid. The R_F value of authentic D(+)-apiose was 0·26 for (*a*), but only 0·04 in (*b*). This showed that the sugar present was rhamnose, not apiose.

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[3] Anderson and Greenwood, *J.*, 1955, 3016.
[4] McCready, Swenson, and Maclay, *Analyt. Chem.*, 1946, **18**, 290.
[5] Anderson and Greenwood, *J. Sci. Food Agric.*, 1955, **6**, 587.
[6] Jermyn and Isherwood, *Biochem. J.*, 1949, **44**, 402.
[7] Gaillard, *Nature*, 1953, **171**, 1160.
[8] Wylam, *J. Sci. Food Agric.*, 1954, **4**, 167.

47. *The Oxidation of Aromatic Primary Amines with Benzoyl Peroxide.*

By J. T. Edward.

The oxidation of *N*-substituted anilines with benzoyl peroxide affords *o*-benzamidophenols in yields of up to 40%.[1,2] However, only low yields of *o*-benzamidophenols have now been obtained from the following primary amines: *o*- and *m*-toluidine, 2 : 4 : 1- and 2 : 5 : 1-xylidine, *p*-bromo-, *p*-chloro-, and 2 : 4-dichloro-aniline. 2-Benzamido-5-bromo-, -5-chloro-, and -3 : 5-dichloro-phenols from the last three amines are new; the structures of the last two were proved by converting them into 6-chloro- and 4 : 6-dichloro-2-phenylbenzoxazole respectively. No phenol was isolated on oxidation of aniline, *p*-toluidine, 2 : 6 : 1-xylidine, *p*-anisidine, or 2 : 4 : 6-tribromoaniline.

The neutral and the basic fractions from these reactions were complex mixtures, from which the azo-compound and, in most instances, the *N*-arylbenzamide were obtained by chromatography on alumina. Smaller amounts of more complex coloured products were also separated by chromatography; their structures are being investigated.

The isolation of azobenzene and benzanilide from the reaction product of aniline with benzoyl peroxide has been reported by Horner and Schwenk.[3] The formation of *N*-arylbenzamides indicates that benzoyl peroxide, besides reacting with amines by a free-radical mechanism,[2,3] undergoes the heterolytic reaction: $Ar{\cdot}NH_2 + Bz_2O_2 \longrightarrow Ar{\cdot}NHBz + BzO_2H$.

Experimental.—Isolation of phenols. Oxidation of the amines by an equimolar amount of benzoyl peroxide in benzene solution at 5°, as judged by the heat evolution and extent of darkening of the solution, was usually complete in less than 10—20 min., although the solutions were usually kept at room temperatures for several hours. However, the less basic amines were oxidized slowly (cf. Horner and Scherf [4]); the solutions containing 2 : 4-dichloro- and 2 : 4 : 6-tribromo-aniline were refluxed for 2 and 6 hr. respectively. The solutions were extracted with sodium hydrogen carbonate to remove benzoic acid (65—80% yields), then with sodium hydroxide to remove phenol. The phenols, all crystallized from aqueous alcohol or acetone, are tabulated.

Amine oxidised *	Phenol *	Yield (%)	M. p. †	Formula		C (%)	H (%)
o-Toluidine	2-Benzamido-*m*-cresol	2	185° (189) [5]	$C_{14}H_{13}O_2N$	Found	74·1	5·7
					Calc.	74·0	5·7
m-Toluidine	2-Benzamido-*p*-cresol	<1	184 (191) [6]	—	—	—	—
2 : 4 : 1-Xylidine ...	2-Benzamido-3 : 5 : 1-xylenol	5	209—210 (211—212) [7]	—	—	—	—
2 : 5 : 1-Xylidine ...	2-Benzamido-3 : 6 : 1-xylenol	12	209—212 (210—211) [8]	$C_{15}H_{15}O_2N$	Found	74·8	6·3
					Calc.	74·7	6·2
p-Bromoaniline ...	2-*Benzamido-5-bromo-phenol*	5	241—242	$C_{13}H_{10}O_2NBr$	Found	53·9	3·5
					Reqd.	53·4	3·5
p-Chloroaniline ...	2-*Benzamido-5-chloro-phenol*	6	231—232	$C_{13}H_{10}O_2NCl$	Found	63·2	3·8
					Reqd.	63·0	4·1
2 4-Dichloroaniline	2-*Benzamido*-3 : 5-*di-chlorophenol*	7	167—170	$C_{13}H_9O_2NCl$	Found	55·8	3·3
					Reqd.	55·4	3·2

* NH_2 and OH = 1. † M. p.s in parentheses are from the literature.

6-Chloro-2-phenylbenzoxazole, sublimed from a mixture of equal parts of 2-benzamido-5-chlorophenol and phosphoric oxide heated to 230°/15 mm., crystallized from aqueous acetone as needles, m. p. 98—100° (Found: C, 68·0; H, 3·2. $C_{13}H_8ONCl$ requires C, 68·0; H, 3·5%).

[1] Gambarjan, *Ber.*, 1909, **42**, 4003.
[2] Edward, *J.*, 1954, 1464.
[3] Horner and Schwenk, *Annalen*, 1950, **566**, 69.
[4] Horner and Scherf, *ibid.*, 1951, **573**, 35.
[5] Gibson, *J.*, 1923, 1269.
[6] Von Auwers and Czerny, *Ber.*, 1898, **31**, 2692.
[7] Von Auwers and Borsche, *Ber.*, 1915, **48**, 1698.
[8] Von Auwers and Schornstein, *Fortschr. Chem. Phys. phys. Chem.*, 1924—1926, **18**, 42; *Chem. Zentr.*, 1924, II, 2269.

4 : 6-*Dichloro*-2-*phenylbenzoxazole*, prepared as above from 2-benzamido-3 : 5-dichlorophenol, crystallized from aqueous acetone in needles, m. p. 133—135° (Found : C, 59·9; H, 3·3. $C_{13}H_7ONCl_2$ requires C, 59·1; H, 2·7%).

Chromatographic separation of the neutral products. After removal of benzoic acid and phenols, the benzene solutions were dried (Na_2SO_4), concentrated at reduced pressure, and chromatographed on alumina. The column was developed with benzene containing increasing proportions of chloroform. The azo-compounds invariably were the first band. Yields were as follows : azobenzene, m. p. 66°, 20%; 2 : 2′-dimethylazobenzene, m. p. 51—53°, 12%; 3 : 3′-dimethylazobenzene, m. p. 53—54°, 21%; 4 : 4′-dimethylazobenzene, m. p. 141—142°, 5%; 2 : 2′ : 4 : 4′-tetramethylazobenzene, m. p. 124—126°, 14%; 2 : 2′ : 5 : 5′-tetramethylazobenzene, m. p. 115—117°, 14%; 2 : 2′ : 6 : 6′-*tetramethylazobenzene*, m. p. 46—47° (Found : C, 80·2; H, 7·6. $C_{16}H_{18}N_2$ requires C, 80·6; H, 7·6%), <1%; 4 : 4′-dichloroazobenzene, m. p. 186—187°, 15%; 2 : 2′ : 4 : 4′-tetrachloroazobenzene, m. p. 162—163°, 5%; 4 : 4′-dibromoazobenzene, m. p. 204—208° (Found : C, 42·7; H, 2·4. Calc. for $C_{12}H_8N_2Br_2$: C, 42·4; H, 2·4%), 5%; 2 : 2′ : 4 : 4′ : 6 : 6′-hexabromoazobenzene, m. p. 212—213°, 13%; 4 : 4′-dimethoxyazobenzene, m. p. 161—162°, 10%. The m. p.s and colours of the compounds, and the colours of their solutions in concentrated sulphuric acid, agreed reasonably well with those reported in the literature.

The following benzanilides were obtained on further elution of the chromatograms : benzanilide, m. p. 160—161°, 28%; benzo-*m*-toluidide, m. p. 125°, 4%; benzo-*p*-toluidide, m. p. 157—158°, 4%; benzo-2 : 4 : 1-xylidide, m. p. 185—187°, 2%; benzo-2 : 5 : 1-xylidide, m. p. 135°; *N*-benzoyl-*p*-chloroaniline, m. p. 190—191° (Found : C, 67·9; H, 4·1. Calc. for $C_{13}H_{10}ONCl$: C, 67·4; H, 4·4%), 5%; and -*p*-bromoaniline, m. p. 206—208° (Found : C, 56·5; H, 3·9. Calc. for $C_{13}H_{10}ONBr$: C, 56·5; H, 3·7%), 19%; and benzo-*p*-anisidide, m. p. 153—154°.

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