Note

3-*O*-Methyl-D-allose and a facile route to 2- and 3-*O*-methyl-D-riboses

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Recent observations that D-ribose stimulates the secretion of insulin[1] have provided the impetus for exploring economical manufacturing processes for this sugar. As one potential route to D-ribose, the degradation of D-allose is very attractive, since oxidation procedures[2] newly developed greatly facilitate the preparation of D-allose. For example, D-allose can be prepared with comparative ease from some disaccharides through biological oxidation[3] and also from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose‡ through oxidation with ruthenium tetraoxide[4] or methyl sulfoxide[5].

In the previous paper[6] the authors discussed the diisopropylidene acetals of D-allose and D-*ribo*-hexulose. In continuation of the previous work on D-allose derivatives, we now describe a synthesis of 3-*O*-methyl-D-allose (**3**), together with a facile route to 2- and 3-*O*-methyl-D-riboses (**6** and **15**) starting from **3** and 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-allofuranose (**12**). Methylation of 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**1**) with methyl sulfate and sodium hydroxide in acetone gave syrupy 1,2:5,6-di-*O*-isopropylidene-3-*O*-methyl-α-D-allofuranose (**2**) in good yield. Hydrolysis of the methyl ether **2** with a cation-exchange resin gave crystalline 3-*O*-methyl-β-D-allopyranose (**3**) in high yield, further characterized as its crystalline *p*-toluenesulfonylhydrazone (**5**). Compound **3** mutarotated from +3.9 to +17.4° during 19 h and also gave crystalline 1,2,4,6-tetra-*O*-benzoyl-3-*O*-methyl-β-D-allopyranose (**4**) upon treatment with benzoyl chloride in pyrdine at low temperature. The n.m.r. spectrum of **4** shows a $J_{1,2}$ coupling constant of about 8 Hz, suggesting the *C1* (D) conformation and the β configuration[8].

In the course of the oxidation with periodic acid under controlled conditions[9], compound **3** consumed one mole of oxidant and gave syrupy 2-*O*-methyl-D-ribose (**6**), which was also characterized as its known[10] *p*-toluenesulfonylhydrazone (**7**). The Ruff degradation[11] was applied on a preparative scale to 3-*O*-methyl-D-allose (**3**). Thus compound **3** was oxidized with bromine to calcium 3-*O*-methyl-D-allonate which was, without further purification, converted into the ether **6** in 52% yield

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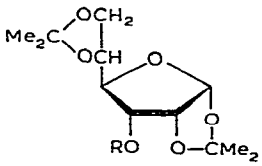
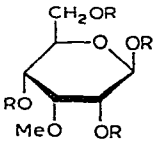
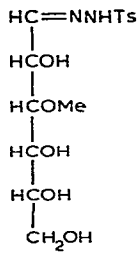
‡For the oxidation of 1,2:5,6-di-*O*-cyclohexylidene-α-D-glucofuranose, see ref. 7.

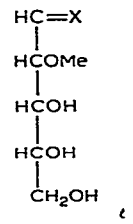


1 R = H
2 R = Me

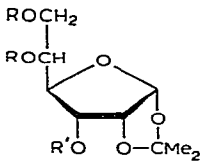


3 R = H
4 R = Bz

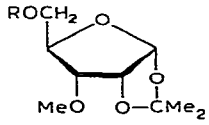




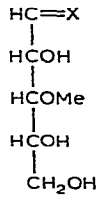
6 X = O
7 X = NNHTs



8 R = H R' = Me
9 R = R' = H
10 R = R' = Ac
11 R = R' = Bz



12 R = H
13 R = Bz
14 R = Ts



15 X = O
16 X = NNHTs

(based on **3**). Compound **6** is an important starting material for the preparation of nucleosides, since this ether is found in RNA from a variety of sources[12].

Partial hydrolysis of compound **2** with cation-exchange resin under mild conditions gave crystalline 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-allofuranose (**8**) in 70% yield. On the other hand, partial hydrolysis of diacetal **1** under the same conditions gave 1,2-*O*-isopropylidene-α-D-allofuranose[13] (**9**) in only 28% yield. The difference in yields between **8** and **9** is probably due to the facile migration[6] of the 1,2-acetal group of diacetal **1**. The acetate (**10**) and benzoate (**11**) of **9** were prepared by the action of acetic anhydride or benzoyl chloride in pyridine in the usual way.

The acetal **8** gave crystalline 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-ribofuranose (**12**) in 80% yield after oxidation with sodium periodate and subsequent reduction with sodium borohydride. Benzoylation and tosylation of **12** in the usual way gave the 5-benzoate (**13**) and the 5-*p*-toluenesulfonate (**14**), respectively, in good yield.

Removal of the protecting group from **12** gave syrupy 3-*O*-methyl-D-ribose (**15**). For characterization of **15**, the crystalline *p*-toluenesulfonylhydrazone (**16**) was prepared in the usual manner.

The literature records relatively few reports dealing with the preparation of 2- and 3-*O*-methylriboses. Thus, apart from the definitive syntheses of 2-*O*-methyl-D-ribose through the addition of methoxide to D-*erythro*-3,4,5-triacetoxy-1-nitro-1-pentene[10], 2-*O*-methyl-L-ribose through the methylation of benzyl 3,4-*O*-isopropylidene-β-L-ribopyranoside[14], and 3-*O*-methyl-D-ribose through the methylation of 1,2,4-*O*-orthobenzoyl-α-D-ribopyranose[15], preparations of these ethers have depended

on partial methylation[16] or have been carried out on a small scale suitable only for chromatographic identification[17].

The methods described here thus provide convenient preparations of 2- and 3-*O*-methyl-D-riboses. Moreover, our method should also be effective for preparation of D-ribose derivatives labeled with deuterium or tritum at C-2, C-3, or C-5 of D-ribose, when sodium borodeuteride or tritiated sodium borohydride is applied for reduction of the intermediate 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose and 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-*ribo*-pentodialdo-1,4-furanose.

EXPERIMENTAL

General. — Melting points are uncorrected. Solutions were evaporated on a rotary evaporator at <40° under diminished pressure. I.r. spectra were recorded for Nujol mulls with a Hitachi spectrometer. N.m.r. spectra were recorded at 60 MHz with a Hitachi H-60 spectrometer. Tetramethylsilane was used as the internal standard in chloroform-*d*. Chemical shifts are given on the τ scale. T.l.c. on Silica Gel GF (E. Merck, Darmstadt, Germany) was performed with solvent systems (*A*) 4:1 (v/v) benzene–ether, and (*B*) 4:1 petroleum ether–ether. Detection was effected with sulfuric acid or u.v. light (short wavelength). Paper chromatography was conducted on Whatman No. 1 paper with the following solvent systems; 3:1:1 (v/v) propyl alcohol–28% ammonia solution–water; and 14:3:3 ethyl acetate–acetic acid–water. Spots were detected by periodate–benzidine.

1,2:5,6-Di-O-isopropylidene-3-O-methyl-α-D-allofuranose (**2**). — 1,2:5,6-Di-*O*-isopropylidene-α-D-allofuranose (**1**, 5.0 g, m.p.[5] 74–75°) was dissolved in acetone (75 ml) and treated with powdered sodium hydroxide (7.5 g). While the mixture was being stirred, methyl sulfate (5 ml) was added dropwise at 50°, and the mixture was refluxed for 1 h. The resultant precipitate was filtered off and washed with acetone (3 × 30 ml). Evaporation of the filtrate gave a yellowish syrup that was homogeneous, by t.l.c., and was distilled twice for analysis; yield 3.8 g (72%), b.p. 120–125° at 10^{-2} torr, $[\alpha]_D^{20}$ +90.0° (*c* 1.4, chloroform); n.m.r. data: τ 4.62 (1-proton doublet, $J_{1,2}$ ~4.5 Hz, H-1), 5.34 (1-proton triplet, H-2), 5.50–6.42 (5-proton multiplet, H-3,4,5,6,6'), 6.55 (3-proton singlet, OMe), 8.45, 8.58 (two 3-proton singlets, C-Me), 8.76 (6-proton singlet, C-Me).

Anal. Calc. for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08. Found: C, 56.88; H, 8.02.

3-O-*Methyl-β-D-allopyranose* (**3**). — 1,2:5,6-di-*O*-isopropylidene-3-*O*-methyl-α-D-allofuranose (4.5 g) was heated in water (100 ml) with Amberlite IR-120 (H^+) resin (10 ml) for 45 min at 80°. The resin was removed and washed with water (3 × 20 ml). The filtrate and washings were concentrated to give a crystalline mass, which was recrystallized from ethanol; yield 2.7 g (84%), m.p. 112–114°, $[\alpha]_D^{20}$ +3.9° (6 min) to +17.4° (19 h) (*c* 1.0, water).

Anal. Calc. for $C_7H_{14}O_6$: C, 43.29; H, 7.27. Found: C, 43.33; H, 7.20.

1,2,4,6-Tetra-O-benzoyl-3-O-methyl-β-D-allopyranose (**4**). — To a cooled mix-

ture of pyridine (15 ml) and benzoyl chloride (2.5 ml) at 0° was added **3** (800 mg) with vigorous stirring. After being kept in an ice–bath for 2 h, the reaction mixture was kept overnight at room temperature. The mixture was processed in the usual way to yield the benzoate; yield 1.96 g (78%), m.p. 112–114°, $[\alpha]_D^{20}$ +3.4° (*c* 1.8, chloroform); n.m.r. data: τ 1.85–2.75 (20-proton multiplet, aromatic protons), 3.35 (1-proton doublet, $J_{1,2}$ ~8 Hz, H-1), 4.45–4.80 (2-proton multiplet, H-2,3), 5.10–5.75 (4-proton multiplet, H-4,5,6,6'), 6.45 (3-proton singlet, OMe).

Anal. Calc. for $C_{35}H_{30}O_{10}$: C, 68.84; H, 4.88. Found: C, 68.62; H, 4.88.

3-O-Methyl-D-allose p-*toluenesulfonylhydrazone* (**5**). — Compound **3** (500 mg) and *p*-toluenesulfonylhydrazide (500 mg) in alcohol (10 ml) were refluxed for 45 min. The solvent was removed and the resulting syrup was dissolved in 1:1 (v/v) ethanol–ethyl acetate (5 ml). The precipitate was collected and washed with cold ethyl acetate (5 ml). Recrystallization from ethyl acetate gave the hydrazone; yield 600 mg (64%), m.p. 148–150°, $[\alpha]_D^{20}$ −23.4° (*c* 1.7, pyridine).

Anal. Calc. for $C_{14}H_{22}N_2O_7S$: C, 46.39; H, 6.12; N, 7.73. Found: C, 46.44; H, 6.02; N, 7.78.

2-O-Methyl-D-ribose (**6**). — *A. Periodate oxidation of* **3**. The methyl ether **3** (600 mg) was added to a solution of periodic acid (0.1M, 50 ml) that was kept at 5°. The periodate consumption reached a constant value of 1.04 moles per mole of the sugar after 4 h. The solution was treated with dilute barium hydroxide until slightly alkaline and the excess alkali was neutralized with carbon dioxide. The precipitated barium salts were removed and concentrated to a syrup. The residue was extracted with ethanol (3 × 20 ml) and the solvent was evaporated to afford a syrup that was dissolved in water. The solution was deionized by passing it through columns of Amberlite IR-120 (H^+) (20 ml) and IRA-410 (OH^-) (20 ml) resins, respectively. Evaporation of the effluent gave 2-*O*-methyl-D-ribose; yield 390 mg (77%), $[\alpha]_D^{20}$ −30.2° (*c* 3.4, methanol) [Lit., $[\alpha]_D$ −32° (*c* 1.09, methanol)[16] and $[\alpha]_D^{25}$ −22° (*c* 3.4, methanol)[10]].

B. Ruff degradation of **3**. Compound **3** (10.0 g) was dissolved in water (60 ml) and bromine (20 g) was added at room temperature. The mixture was kept for 72 h at room temperature with occasional shaking. Excess bromine was evaporated off on a steam-bath, and the solution was diluted with water to 200 ml and neutralized with lead carbonate (50 g). The precipitate was removed by filtration and washed with water (4°, 20 ml). The solution was saturated with hydrogen sulfide and the precipitate removed. Calcium carbonate (5 g) was added to the filtrate and the mixture was heated for 30 min on a steam-bath. The cooled mixture was filtered, and the precipitate was washed with water (2 × 20 ml). The solution was concentrated to a syrup that was triturated with ethanol (20 ml) to give calcium 3-*O*-methyl-D-allonate (10.0 g). The calcium salt (10.0 g), barium acetate monohydrate (1.3 g), and ferric sulfate (0.6 g) were dissolved in water (200 ml) and, while being stirred, hydrogen peroxide (30%, 15 ml) was added at 40° in two portions. The cooled, dark mixture was treated with carbon and filtered. The filtrate was passed successively through columns of Amberlite IR-120 (H^+) (200 ml) and Amberlite IRA-410 (OH^-) (200 ml) resins.

The effluent was concentrated to a chromatographically homogeneous syrup; yield 4.4 g (52%), $[\alpha]_D^{20}$ −32.4° (*c* 2.3, methanol).

2-O-Methyl-D-ribose p-toluenesulfonylhydrazone (**7**). — The syrupy **6** (500 mg) and *p*-toluenesulfonylhydrazide (500 mg) were heated in ethanol (10 ml) for 45 min under reflux. The precipitate was collected and washed with cold ethanol. Recrystallization from ethanol gave the hydrazone; yield 650 mg (65%), m.p. 142–145°, $[\alpha]_D^{20}$ −8.0° (*c* 1.0, water) [lit., m.p. 145–146°, $[\alpha]_D^{20}$ −8° (*c* 1.0, water)[10]].

Anal. Calc. for $C_{13}H_{20}N_2O_6S$: C, 46.97; H, 6.06; N, 8.42. Found: C, 46.88; H, 6.12; N, 8.17.

1,2-O-Isopropylidene-3-O-methyl-α-D-allofuranose (**8**). — The acetal **2** (15.0 g) was suspended in water (200 ml) and stirred with Amberlite IR-120 (H^+) (30 ml) for 45 min at 24°. The resin was removed and washed with water (3 × 20 ml). The solution was extracted with ether (30 ml) to remove unchanged starting material and the aqueous phase was concentrated to dryness. Recrystallization from ethanol–toluene gave the title compound; yield 9.0 g (70%), m.p. 120–121°, $[\alpha]_D^{20}$ +108.8° (*c* 1.0, water).

Anal. Calc. for $C_{10}H_{18}O_6$: C, 51.27; H, 7.75. Found: C, 51.20; H, 7.75.

1,2-O-Isopropylidene-α-D-allofuranose (**9**). — The diacetal **1** (5.0 g) was suspended in water (150 ml) and stirred with Amberlite IR-120 (H^+) (10 ml) for 45 min. at 24° The resin was removed and washed with water. The combined mixture was extracted with ether (20 ml), and the aqueous solution was evaporated to dryness. The resulting crystals were extracted with acetone (3 × 20 ml). The insoluble crystals were D-allose; yield 1.8 g (52%) m.p. 126–128° after recrystallization from ethanol. The acetone solution was evaporated to dryness and the residue recrystallized from ethyl acetate; yield 1.2 g (28%), m.p. 129–130°, $[\alpha]_D^{20}$ +47.8° (*c* 1.4, water) [lit., m.p. 129–130°, $[\alpha]_D^{20}$ +48° in water[13]].

Anal. Calc. for $C_9H_{16}O_6$: C, 49.08; H, 7.32. Found: C, 49.12; H, 7.26.

3,5,6-Tri-O-acetyl-1,2-O-isopropylidene-α-D-allofuranose (**10**). — The monoacetal **9** (1.0 g) was acetylated with acetic anhydride and pyridine. After recrystallization from ether–ligroin, 1.2 g (76%) of the acetate was obtained, m.p. 79–81°, $[\alpha]_D^{20}$ +111.1° (*c* 1.8, chloroform); n.m.r. data: τ 4.24 (1-proton doublet, $J_{1,2}$ ~3.5 Hz, H-1), 4.60–4.90 (1-proton multiplet, H-2), 5.00–6.10 (5-proton multiplet, H-3,4,5,6,6'), 7.90 (3-proton singlet, OAc), 7.95 (6-proton singlet, two OAc groups), 8.45, 8.66 (two 3-proton singlets, C-Me).

Anal. Calc. for $C_{15}H_{22}O_9$: C, 52.02; H, 6.40. Found: C, 52.06; H, 6.48.

3,5,6-Tri-O-benzoyl-1,2-O-isopropylidene-α-D-allofuranose (**11**). — The monoacetal **9** (1.0 g) was benzoylated with benzoyl chloride and pyridine in the usual manner. After recrystallization from ethanol, 2.0 g (83%) of the benzoate was obtained; m.p. 116–118°, $[\alpha]_D^{20}$ +107.9° (*c* 2.4, chloroform); n m.r. data: τ 1.90–2.95 (15-proton multiplet, aromatic protons), 4.15 (1-proton doublet, $J_{1,2}$ ~4.5 Hz, H-1), 4.16–5.76 (6-proton multiplet, H-2,3,4,5,6,6'), 8.50, 8.72 (two 3-proton singlets, C-Me).

Anal. Calc. for $C_{30}H_{28}O_9$: C, 67.66; H, 5.30. Found: C, 67.42; H, 5.18.

1,2-O-Isopropylidene-3-O-methyl-α-D-ribofuranose (**12**). — 1,2-*O*-Isopropyli-

dene-3-*O*-methyl-α-D-allofuranose **8** (5.0 g) was dissolved in water (100 ml) and treated with sodium periodate (4.5 g) for 30 min at room temperature. The solution was evaporated to dryness and the residues were extracted with dichloromethane (3 × 30 ml). The extract was evaporated again to dryness. The syrup was dissolved in water (30 ml) and sodium borohydride (2.0 g) was added to effect reduction at room temperature. After being kept for 2 h at room temperature, acetic acid was added carefully to neutralization and the solution was evaporated to dryness. Boric acid was removed by evaporation of methanol (5 × 20 ml) from the residue and the residue was extracted with ether. Removal of the ether gave a crystalline mass that was recrystallized from cyclohexane; yield 3.8 g (80%), m.p. 56–58°, $[\alpha]_D^{20}$ +88.4° (*c* 1.1, chloroform).

Anal. Calc. for $C_9H_{16}O_5 \cdot H_2O$: C, 48.64; H, 8.16. Found: C, 48.59; H, 8.18.

The anhydrous form was obtained by heating at 80° under diminished pressure (16 torr) for 8 h, and it had m.p. 74–76°, $[\alpha]_D^{20}$ +100.0° (*c* 1.3, chloroform); n.m.r. data: τ 4.20 (1-proton doublet, $J_{1,2}$ ~3.5 Hz, H-1), 5.22 (1-proton triplet, H-2), 5.75–6.35 (4-proton multiplet, H-3,4,5,5′), 6.40 (3-proton singlet, OMe), 8.25, 8.45 (two 3-proton singlets, C-Me).

5-O-Benzoyl-1,2-O-isopropylidene-3-O-methyl-α-D-ribofuranose (**13**). — The anhydrous form of 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-ribofuranose (**12**, 1.0 g) was treated with benzoyl chloride and pyridine. Purification in the usual way gave, after recrystallization from aqueous ethanol, the benzoate; yield 1.1 g (74%), m.p. 74–76°, $[\alpha]_D^{20}$ +75.2° (*c* 1.5, chloroform); n.m.r. data: τ 1.80–2.75 (5-proton multiplet, aromatic protons), 4.20 (1-proton doublet, $J_{1,2}$ ~3.5 Hz, H-1), 5.25–6.40 (5-proton multiplet, H-2,3,4,5,5′), 6.55 (3-proton singlet, OMe), 8.42, 8.65 (two 3-proton singlets, C-Me).

Anal. Calc. for $C_{15}H_{20}O_6$: C, 60.79; H, 6.80. Found: C, 60.74; H, 6.78.

1,2-O-Isopropylidene-3-O-methyl-5-O-tosyl-α-D-ribofuranose (**14**). — The anhydrous form **12** (1.0 g) was sulfonylated with *p*-toluenesulfonyl chloride (2.0 g) in pyridine (10 ml) for 24 h at room temperature. The product was isolated in the usual way. After recrystallization from ethanol, the sulfonate (1.3 g, 68%) had m.p. 108–109° and $[\alpha]_D^{20}$ +60.0° (*c* 1.5, chloroform); n.m.r. data: τ 2.10–2.85 (4-proton multiplet, aromatic protons), 4.25–4.50 (1-proton multiplet, H-1), 5.30–6.40 (6-proton multiplet, H-2,3,4,5,5′), 6.55 (3-proton singlet, OMe), 7.55 (3-proton singlet, Me of Ts), 8.50, 8.68 (two 3-proton singlets, C-Me).

Anal. Calc. for $C_{16}H_{22}O_7S$: C, 51.32; H, 5.29. Found: C, 51.35; H, 5.88.

3-O-Methyl-D-ribose and its p-toluenesulfonylhydrazone (**15** *and* **16**). — Compound **12** (2.0 g) was suspended in water (50 ml) and treated with Amberlite IR-120 (H^+) (5 ml) for 45 min at 80°. The resin was removed and washed with water. The solution was concentrated to a syrup that was chromatographically homogeneous; yield 1.5 g (94%), $[\alpha]_D^{20}$ −20.5° (*c* 3.4, methanol) [lit., $[\alpha]_D^{20}$ +7.5° (*c* 0.6, methanol)]. The syrup (1.0 g) and *p*-toluenesulfonylhydrazide (1.0 g) were heated in ethanol (10 ml) for 45 min on a steam-bath. Removal of the solvent gave the hydrazone; yield 1.3 g (65%), m.p. 132–133°, $[\alpha]_D^{20}$ −45.2° (*c* 2.4, pyridine).

Anal. Calc. for $C_{13}H_{20}N_2O_6S$: C, 46.79; H, 6.06; N, 8.42. Found: C, 46.82; H, 6.22; N, 8.38.

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REFERENCES

1 J. B. Halter, M. Z. Schartz, and F. C. Goetz, *Proc. Soc. Exp. Biol. Med.*, 127 (1968) 1147; H. A. Sloviter and M. R. Petkovic, *Nature*, 221 (1969) 371.
2 R. F. Butterworth and S. Hanessian, *Synthesis*, (1971) 70.
3 M. J. Bernaerts, J. Furnelle, and J. De Ley, *Biochim. Biophys. Acta*, 69 (1969) 322; R. L. Metzenberg and G. A. Marzluf, *Anal. Biochem.*, 13 (1965) 168.
4 P. J. Beynon, P. M. Collins, P. T. Doganges, and W. G. Overend, *J. Chem. Soc.* (*C*) (1966) 1131.
5 W. Sowa and G. H. S. Thomas, *Can. J. Chem.*, 44 (1966) 836; K. Onodera, S. Hirano, and N. Kashimura, *Carbohyd. Res.*, 6 (1968) 276.
6 M. Haga, M. Takano, and S. Tejima, *Carbohyd. Res.*, 14 (1970) 237.
7 K. James, A. R. Tachell, and P. K. Ray, *J. Chem. Soc.* (*C*), (1967) 2681; M. Kawana, H. Ohrui, and S. Emoto, *Bull. Chem. Soc. Japan*, 41 (1968) 2199.
8 R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider *J. Amer. Chem. Soc.*, 80 (1958) 6098.
9 G. W. Huffman, B. A. Lewis, F. Smith, and D. R. Spriestersbach, *J. Amer. Chem. Soc.*, 77 (1955) 4346.
10 J. C. Sowden, M. L. Oftedahl, and A. Kirkland, *J. Org. Chem.*, 27 (1962) 1791.
11 O. T. Schmidt and A. Simon, *J. Prakt. Chem.*, 152 (1939) 190.
12 D. B. Bunn, J. H. Hutchinson, and A. R. Trimm, *Biochem. J.*, 88 (1963) 34p; D. L. Correll, *Phytochemistry*, 4 (1965) 453; E. K. Wagner, S. Penman, and V. M. Ingram, *J. Mol. Biol.*, 29 (1967) 371.
13 P. M. Collins, *Tetrahedron*, 21 (1965) 1809.
14 A. H. Haines and P. R. Lundie, *J. Chem. Soc.* (*C*), (1970) 1691.
15 H. G. Fletcher, Jr. and R. K. Ness, *J. Amer. Chem. Soc.*, 77 (1955) 5337.
16 G. R. Barker, T. M. Noone, D. C. C. Smith, and J. W. Spoors, *J. Chem. Soc.*, (1955) 1327.
17 D. M. Brown, D. I. Magrath, and A. R. Todd, *J. Chem. Soc.*, (1954) 1442; D. Lipkin, W. H. Cooke, and R. Markham, *J. Amer. Chem. Soc.*, 81 (1959) 6198.