1082. *Phenolic Constituents of* Vaccinium Vitis idaea *L.*

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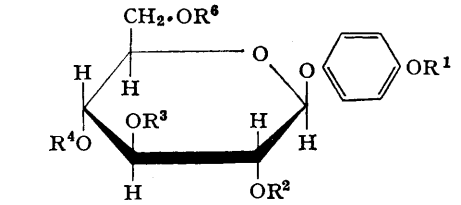
Two compounds isolated from the leaves of the mountain cranberry have been shown to be the 6-*O*-acetyl (II) and 2-*O*-caffeoyl (VIII) derivatives of arbutin.

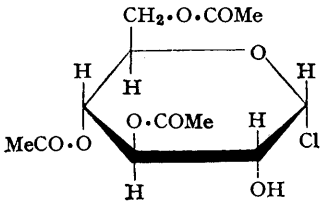
The phenolic glucoside arbutin (quinol β-D-glucoside) (I) is of interest not only in relation to its biogenesis[1] but also taxonomically[2] since its natural distribution is limited to a few plant families such as the *Rosaceae*, *Ericaceae*, and *Saxifragaceae*. Recently, Friedrich isolated pyroside a crystalline mono-*O*-acetyl derivative of arbutin from the leaves of pear[3] (*Pyrus communis*) and mountain cranberry[4] (*Vaccinium vitis idaea* L.), and on the basis of infrared evidence suggested[4] that it was 6-*O*-acetylarbutin (II). During a programme of studies of the phenolic constituents of members of the *Ericaceae* the structure of pyroside has been confirmed and a further acyl derivative of arbutin isolated and identified.

The general structural features of pyroside were confirmed by its conversion on acetylation into arbutin penta-acetate (III) and by its hydrolysis to give arbutin (I). The proton resonance spectrum of pyroside showed the presence of two protons α to the acetate ester group, thus supporting Friedrich's postulated structure (II) which was finally substantiated by synthesis. Tritylation of arbutin followed by treatment with ethyl chloroformate gave a tetra-*O*-ethoxycarbonyl trityl ether which, on the basis of previous work[5] and its proton resonance spectrum, was formulated as (IV). Removal of the trityl group followed by acetylation gave (V) identical with the tetra-*O*-ethoxycarbonyl derivative of natural pyroside. Treatment of (V) with ammonia at 20° gave quinol 6-*O*-acetyl-β-D-glucoside (II) identical with pyroside. The natural product was also produced by variations of methods[6,7] known to produce the 6-*O*-acyl derivatives of glucose and of oligosaccharides containing the D-glucopyranose structure. Thus, controlled de-acetylation of arbutin penta-acetate (III) gave excellent yields of pyroside. In this case, since (V) on similar treatment gave good yields

[1] S. K. Grisdale and G. H. N. Towers, *Nature*, 1960, **188**, 1130.
[2] H. Friedrich, *Planta Med.*, 1956, **4**, 178.
[3] H. Friedrich, *Pharmazie*, 1960, **15**, 319.
[4] H. Friedrich, *Naturwiss.*, 1961, **48**, 304.
[5] B. Helferich, *Adv. Carbohydrate Chem.*, 1948, **3**, 79.
[6] R. B. Duff, *J.*, 1957, 4730.
[7] Y. Z. Frohwein and J. Liebowitz, *Nature*, 1960, **186**, 153; *Bull. Res. Council Israel*, 1963, **11**, *A*, 330.

of pyroside, the reaction most probably proceeds to the desired product because of the more ready base-catalysed hydrolysis of the secondary acetate functions rather than an initial de-acetylation at the 6-position and subsequent successive migrations of the remaining acetate groups to the primary alcoholic group. Pyroside was also formed by treatment of arbutin with 50% acetic acid at 37° in a manner analogous to that used by Duff[6] to prepare 6-*O*-acetyl-D-glucose. Not surprisingly, therefore, refluxing arbutin in moist ethyl acetate also gave quinol 6-*O*-acetyl-β-D-glucoside, but the possibility that pyroside was an artefact formed during the preparation of the plant extract was excluded by the demonstration of its presence in ether extracts of mountain cranberry leaves.





(X)

(I) All R's = H
(II) $R^1 = R^2 = R^3 = R^4 = H$, $R^6 = COMe$
(III) All R's = COMe
(IV) $R^1 = R^2 = R^3 = R^4 = CO_2Et$, $R^6 = CPh_3$
(V) $R^1 = R^2 = R^3 = R^4 = CO_2Et$, $R^6 = COMe$
(VI) $R^1 = R^2 = R^3 = R^4 = H$, $R^6 = CO{\cdot}CH{:}CH{\cdot}C_6H_3(OH)_2$-3,4
(VII) $R^1 = R^2 = R^3 = R^4 = COMe$, $R^6 = H$
(VIII) $R^1 = R^3 = R^4 = R^6 = H$, $R^2 = CO{\cdot}CH{:}CH{\cdot}C_6H_3(OH)_2$-3,4
(IX) $R^1 = R^3 = R^4 = R^6 = COMe$, $R^2 = H$

Paper-chromatographic analysis of mountain cranberry leaf extracts revealed the presence of a further compound in addition to arbutin and pyroside, giving the distinctive blue colouration with Gibbs reagent and which also displayed under ultraviolet light a fluorescence typical of caffeic (3,4-dihydroxycinnamic) esters. This substance was isolated in a crystalline form (0·02%) and its elemental analysis and spectroscopic properties favoured its formulation as a mono-*O*-caffeoyl derivative of arbutin. Support for this structure was obtained by the preparation of a hexa-acetate and by a paper-chromatographic analysis of the course of its acid hydrolysis. Glucose, caffeic acid, and quinol were thus identified as products of complete breakdown, and along with arbutin and an *O*-caffeoyl derivative of glucose (showing a positive reaction to aniline hydrogen phthalate) as products of partial hydrolysis. By analogy with pyroside, it was thought that the position of attachment of the caffeoyl group would be to the primary alcoholic group of arbutin, but the hexa-acetate of quinol 6-*O*-caffeoyl-β-D-glucoside (VI), prepared by condensing 3,4-diacetoxycinnamoyl chloride with *O*-acetylquinol 2,3,4-tri-*O*-acetyl-β-D-glucoside (VII), differed significantly from the acetate of the natural product. This observation was supported by the proton resonance spectrum of the natural product which showed the presence of only one proton α to the caffeoyl group.

The structure of the natural product was deduced from an unusually facile migration of the *O*-caffeoyl group on treatment with ammonia at 0°. Paper-chromatography showed that an intermediate was rapidly formed (1 min.) which was equally rapidly transformed into a stable end-product (5 min.) retaining the colour reactions and fluorescence associated with an *O*-caffeoyl derivative of arbutin. Previous work on acyl migrations in carbohydrate chemistry indicates[8] that this process nearly always occurs with migration towards the terminal 6-position of glucose, and that where an acyl group is attached to the 6-position this is not normally prone to rearrangement. Sufficient material was not available for detailed

[8] J. M. Sugihara, *Adv. Carbohydrate Chem.*, 1953, **8**, 1.

analysis of the rearrangement but since the final product was chromatographically indistinguishable from the product of deacetylation of the hexa-acetate of (VI) it was therefore assigned, on the basis of these arguments, the structure of 6-*O*-caffeoylarbutin (VI). The observed migration of the caffeoyl group was thus tentatively identified as being in the sequence 3 → 4 → 6 or 2 → 3 → 6, of which the latter was favoured on steric grounds. Confirmation of the structure of the natural glucoside therefore as 2-*O*-caffeoylarbutin (VIII) was obtained by synthesis of the hexa-acetate of (VIII). Koenigs–Knorr condensation of 3,4,6-tri-*O*-acetyl-α-D-glucosyl chloride[9] (X) and mono-*O*-acetylquinol gave in poor yield *O*-acetylquinol 3,4,6-tri-*O*-acetyl-β-D-glucoside (IX) whose structure was confirmed by acetylation to give arbutin penta-acetate (III), by formation of a monobenzoate, and by methylation followed by acid hydrolysis to give 2-*O*-methyl-D-glucose identified paper-chromatographically and by paper electrophoresis in germanate buffer.[10] Condensation of 3,4-diacetoxycinnamoyl chloride with (IX) gave the hexa-acetate of 2-*O*-caffeoylarbutin (VIII) identical with the acetate of the natural glucoside. Attempts to prepare the latter by a carefully controlled de-acetylation of the hexa-acetate were ambiguous owing to the concomitant migration of the caffeoyl group, and compounds provisionally identified paper-chromatographically as 3- and 6-*O*-caffeoylarbutin were present amongst the products of reaction. Further work on this aspect of the problem is in progress.

Experimental

Paper chromatography was carried out using Whatman No. 1 paper in the solvent systems: A, 6% aqueous acetic acid; and B, butan-2-ol–acetic acid–water (14:1:5) at 20 ± 3°. Arbutin and arbutin derivatives with a free phenolic hydroxyl group on the aglucone were detected by their blue colourations when sprayed with a 1% methanolic solution of 2,6-dibromobenzoquinone 4-chloroimide (Gibbs reagent) followed by a saturated solution of sodium hydrogen carbonate.[11] Caffeic esters were revealed by their blue fluorescence under ultraviolet light, changing to green in the presence of ammonia vapour, and by the general *vic*-dihydroxyphenol spray[12] of ferric chloride–potassium ferricyanide (0·2% w/v solutions; 1:1).

Countercurrent distributions were carried out between ethyl acetate and water, and the distribution analysed by paper chromatography and/or measurement of the optical density at 320 mμ of aliquots (1 c.c. from the upper phase of each tube diluted with 1 c.c. of ethanol).

Proton magnetic resonance spectra were measured at 60 Mc./sec., using acetonitrile as internal standard. Arbutin and its derivatives were evaporated with deuterated water before dissolution in this solvent or acetone.

Isolation of Phenolic Constituents.—Freshly gathered cranberry (*Vaccinium vitis idaea* L.) leaves (1500 g.) were homogenised with water (4 × 1000 c.c.) and the suspension filtered successively through glass wool and a layer (10 cm.) of iron-free cellulose in a Buchner funnel. The resultant solution was concentrated to 250 c.c. at 30°, and extracted with ethyl acetate (15 × 200 c.c.). Removal of the ethyl acetate at 30° gave a brown gum which was analysed by paper chromatography (solvents A and B) (Table). The gum was shaken with 6% aqueous acetic acid

	R_F		Spray		U.v.	
Compound	A	B	$FeCl_3$–$K_3FeC_6N_6$	Gibbs	NH_3	Identification
1	0·83	0·51	+	Blue	Absorbs	Arbutin
2	0·85	0·69	+	Blue	Absorbs	Pyroside
3	0·60	0·70	+	Brown	Green	Unknown
4	0·65	0·81	+	Blue–green	Green	Unknown
5	0·67	0·85	+	Blue–green	Blue	Unknown
6	0·70	0·90	+	Purple	Absorbs	Quinol
7	0·55	0·60	—	—	Blue	Unknown
8	0·50	0·77	+	Brown	Green	Unknown
9	0·40	0·88	+	Brown	Blue	Unknown
10	0·30	0·68	+	Brown	Yellow	Flavonoid

[9] R. U. Lemieux and G. Huber, *Canad. J. Chem.*, 1953, **31**, 1040.
[10] B. Lindberg and B. Swan, *Acta Chem. Scand.*, 1960, **14**, 1043.
[11] F. E. King, T. J. King, and L. C. Manning, *J.*, 1957, 563.
[12] K. S. Kirby, E. Knowles, and T. White, *J. Soc. Leather Trades' Chemists*, 1953, **37**, 283.

(100 c.c.) for 1 hr., the solution filtered, and the filtrate applied to a cellulose column (80 × 5·5 cm.) packed in the same solvent. Elution was carried out with 6% aqueous acetic acid, and fractions (15 c.c.) were collected and analysed by paper chromatography in solvent systems A and B. Concentration (30°) of the fractions 1—66 gave a gum which consisted predominantly of arbutin and pyroside and was subjected to countercurrent distribution between ethyl acetate and water (60 transfers, phase volume 40 c.c.). Analysis by paper chromatography (solvent B), followed by concentration of tubes 2—8, gave arbutin as needles (0·25 g.) (from water), m. p. and mixed m. p. 200°, K(ethyl acetate:water), 0·10. Tubes 10—18 gave pyroside as needles (0·20 g.) (from water), m. p. 212° (lit.,[3] 214—216°) (Found: C, 53·3; H, 5·8; *O*-acetyl, 14·5. Calc. for $C_{14}H_{18}O_8$: C, 53·5; H, 5·7; *O*-acetyl, 14·8%), $[\alpha]_D^{23}$ −58·8° (*c* 2 in water), K(ethyl acetate:water), 0·33, $\nu_{max.}$ (Nujol) 1750, 3350, and 3450 cm.$^{-1}$. Concentration of fractions 76—135 gave a gum consisting of compounds **3**, **4**, **5**, and quinol which was subjected to countercurrent distribution between ethyl acetate and water (50 transfers, phase volume 40 c.c.). Tubes 22—25 gave compound **3** as an amorphous powder (0·05 g.). Tubes 34—39 gave *compound* **4** as prisms (0·3 g.) (from acetone–benzene), m. p. 165° (Found: C, 57·7; H, 5·3. $C_{21}H_{22}O_{10}$ requires C, 58·0; H, 5·0%), $\nu_{max.}$ (Nujol) 1640, 1710, and 3350 cm.$^{-1}$, K(ethyl acetate:water), 2·5. Tubes 47—50 gave quinol, prisms (0·1 g.) (from acetone–benzene), m. p. and mixed m. p. 174°.

Hydrolysis of Pyroside.—(*a*) Pyroside (0·05 g.) dissolved in 2N-ammonium hydroxide (5 c.c.) was left at 20° for 24 hr., the solvent removed at 30°, and the resultant gum extracted with warm ethyl acetate (5 × 10 c.c.). Removal of the solvent and crystallisation of the residue from water gave arbutin as needles (0·02 g.), m. p. and mixed m. p. 200°.

(*b*) A solution of pyroside (0·01 g.) in N-hydrochloric acid (3 c.c.) was refluxed for 6 hr.; paper chromatography then showed the presence of glucose and quinol.

Acetylation of Pyroside.—A solution of pyroside (0·05 g.) and acetic anhydride (2 c.c.) in pyridine (1 c.c.) was left at room temperature for 24 hr., poured into ice-cold water (10 c.c.), and allowed to stand for 1 hr. The precipitate crystallised from ethanol as needles (0·05 g.) of arbutin penta-acetate, m. p. and mixed m. p. 145°.

O-*Ethoxycarbonylquinol* 2,3,4-*Tri*-O-*ethoxycarbonyl*-6-O-*trityl*-β-D-*glucoside.*—A solution of arbutin (5 g.) and triphenylchloromethane (5 g.) in pyridine (40 c.c.) was shaken at room temperature for 12 hr., and ethylchloroformate (35 c.c.) was added with stirring during 1 hr. The mixture, after standing for 12 hr., was poured into ice–water (1000 c.c.) and stirred for 2 hr. The white granular precipitate was washed with water (2000 c.c.) and crystallised (3×) from ethanol, to give needles (8 g.) of the *glucoside*, m. p. 154° (Found: C, 64·6; H, 6·0. $C_{43}H_{46}O_{15}$ requires C, 64·3; H, 5·7%), $\nu_{max.}$ (Nujol) 705, 745, 785, 840, and 1750 cm.$^{-1}$.

O-*Ethoxycarbonylquinol* 2,3,4-*Tri*-O-*ethoxycarbonyl*-β-D-*glucoside.*—To a solution of *O*-ethoxycarbonylquinol 2,3,4-tri-*O*-ethoxycarbonyl-6-*O*-trityl-β-D-glucoside (10 g.) in glacial acetic acid (50 c.c.) at 15° was added a saturated solution of hydrogen bromide in acetic acid (15 c.c.). The precipitated trityl bromide was filtered off, the filtrate poured into ice–water (500 c.c.), and the solution extracted with chloroform (3 × 500 c.c.). Removal of the chloroform at 30° gave a gum which was thrice crystallised from ethanol, to give the *glucoside* as needles (2 g.), m. p. 129—130° (Found: C, 51·1; H, 5·6. $C_{24}H_{32}O_{15}$ requires C, 51·4; H, 5·7%), $\nu_{max.}$ (Nujol) 1750 and 3500 cm.$^{-1}$. Treatment of the product (0·5 g.) with triphenylchloromethane (0·3 g.) in pyridine (6 c.c.) for 12 hr. gave the 6-*O*-trityl ether (0·6 g.), isolated as described above, m. p. and mixed m. p. 154°.

O-*Ethoxycarbonylquinol* 2,3,4-*Tri*-O-*ethoxycarbonyl*-6-O-*acetyl*-β-D-*glucoside.*—(*a*) To a solution of *O*-ethoxycarbonylquinol 2,3,4-tri-*O*-ethoxycarbonyl-β-D-glucoside (1 g.) in pyridine (5 c.c.) was added acetic anhydride (6 c.c.) and the whole left at room temperature for 24 hr. and poured into ice–water (50 c.c.). The precipitated product gave the *acetate* as needles (0·9 g.), m. p. 88° (from ethanol) (Found: C, 51·9; H, 5·6. $C_{26}H_{34}O_{16}$ requires C, 51·8; H, 5·7%), $\nu_{max.}$ (Nujol) 785, 840, and 1750 cm.$^{-1}$.

(*b*) Ethyl chloroformate (3 c.c.) was added slowly (30 min.) to a solution of pyroside (0·1 g.) in pyridine (2 c.c.) at 0°, and the solution left at room temperature for 24 hr. and poured into ice–water (20 c.c.). The product crystallised to give the glucoside as needles (0·08 g.), m. p. and mixed m. p. 88° (Found: C, 60·0; H, 5·7. Calc. for $C_{26}H_{34}O_{16}$: C, 51·8; H, 5·7%), $\nu_{max.}$ (Nujol) 1750 cm.$^{-1}$.

Quinol 6-O-*Acetyl*-β-D-*glucoside.*—(*a*) To a solution of the above glucoside (1·5 g.) in acetone (5 c.c.) was added a solution of ammonia (*d* 0·88; 3 c.c.) in ethanol (18 c.c.) and the mixture left at 20° for 4 hr. Removal of the solvents at 20° gave a gum which was subjected to countercurrent

distribution between ethyl acetate and water (60 transfers, phase volume 40 c.c.) and the distribution analysed by paper chromatography in solvent system B. Concentration of the contents of tubes 2—8 gave, after crystallisation from water, arbutin (0·1 g.) as needles, m. p. and mixed m. p. 200°. Tubes 10—18, similarly concentrated, gave, after crystallisation from water, quinol 6-*O*-acetyl-β-D-glucoside as needles (0·12 g.), m. p. and mixed m. p. with pyroside, 212° (Found: C, 53·3; H, 5·6; *O*-acetyl, 14·3. Calc. for $C_{14}H_{18}O_8$: C, 53·5; H, 5·7; *O*-acetyl, 14·8%), $\nu_{max.}$ (Nujol) 1750, 3350, and 3450 cm.$^{-1}$, $[\alpha]_D^{23}$ −58·4° (*c* 1·8 in water).

(*b*) Arbutin penta-acetate (5 g.) treated as above gave quinol 6-*O*-acetyl-β-D-glucoside (0·9 g.), m. p. and mixed m. p. with pyroside 212°.

(*c*) A solution of arbutin (2 g.) in aqueous acetic acid (50%; 10 c.c.) was maintained at 37° for 2 days, and the solvent was removed at 30° and the residual gum subjected to countercurrent distribution between ethyl acetate and water (60 transfers, phase volume 40 c.c.). Concentration of tubes 9—17 gave quinol 6-*O*-acetyl-β-D-glucoside (0·2 g.), m. p. and mixed m. p. with pyroside, 212°.

Hydrolysis of Compound 4.—(*a*) The substance (0·02 g.) was refluxed with N-hydrochloric acid and the hydrolysis followed by paper-chromatographic analysis. After 2 hr. the following compounds were identified: glucose, R_F(A) 0·90, R_F(B) 0·20; arbutin, R_F(A) 0·83, R_F(B) 0·70; caffeic acid, R_F(A) 0·33, R_F(B) 0·85; unchanged compound 4, R_F(A) 0·65, R_F(B) 0·81. After 10 hr. only glucose, caffeic acid, and quinol were detected.

(*b*) Compound 4 (0·01 g.) was added to 2N-ammonium hydroxide (3 c.c.) at 0° under nitrogen. The results are discussed on p. 5650.

O-*Acetylquinol* 2,3,4-*Tri*-O-*acetyl*-6-O-*trityl*-β-D-*glucoside*.—A solution of arbutin (5 g.) and triphenylchloromethane (5 g.) in pyridine (50 c.c.) was shaken at room temperature for 12 hr., acetic anhydride (50 c.c.) was added, and the mixture set aside for a further 12 hr. The solution was poured with stirring into ice–water (1000 c.c.) and after 2 hr. the *trityl derivative* was recrystallised from ethanol, to give needles (7·5 g.), m. p. 197—198° (Found: C, 69·2; H, 5·6. $C_{39}H_{36}O_{11}$ requires C, 68·8; H, 5·3%), $\nu_{max.}$ (Nujol) 705, 745, 840, and 1750 cm.$^{-1}$.

O-*Acetylquinol* 2,3,4-*Tri*-O-*acetyl*-β-D-*glucoside*.—A saturated solution of hydrogen bromide in glacial acetic acid (15 c.c.) was added to the above trityl ether (10 g.) in acetic acid (50 c.c.) at 10°. The precipitated trityl bromide was filtered off, the filtrate poured into ice–water (500 c.c.), and the solution extracted with chloroform (3 × 500 c.c.). Removal of the chloroform at 30° gave a gum which, after precipitation from ethanol with water, was crystallised from ethanol (3 ×) to give O-*acetylquinol* 2,3,4-*tri*-O-*acetyl*-β-D-*glucoside* as needles (2·5 g.), m. p. 147—148° (Found: C, 54·7; H, 5·4. $C_{20}H_{24}O_{11}$ requires C, 54·6; H, 5·5%), $\nu_{max.}$ (Nujol) 1750 and 3500 cm.$^{-1}$. Treatment of the product (0·5 g.) with triphenylchloromethane (0·3 g.) in pyridine (6 c.c.) for 12 hr. gave the trityl ether, isolated as described above, m. p. and mixed m. p. 196—197°.

O-*Acetylquinol* 2,3,4-*Tri*-O-*acetyl*-6-O-(3,4-*diacetoxycinnamoyl*)-β-D-*glucoside*.—To a solution of *O*-acetylquinol 2,3,4-tri-*O*-acetyl-β-D-glucoside (2·2 g.) in chloroform (100 c.c.), containing pyridine (15 c.c.) was added during 1 hr. a solution of 3,4-diacetoxycinnamoyl chloride (2·0 g.) in chloroform (25 c.c.). The mixture was left at room temperature for 24 hr. before dilution with chloroform (200 c.c.) and extraction of the organic layer successively with ice-cold 2N-hydrochloric acid (2 × 100 c.c.), saturated sodium hydrogen carbonate solution (2 × 100 c.c.), and water (100 c.c.). After drying ($MgSO_4$) the chloroform was removed and the *product* (2·6 g.) crystallised from ethanol as needles, m. p. 134 and 170° (Found: C, 57·6; H, 5·1. $C_{33}H_{34}O_{16}$ requires C, 57·6; H, 5·1%), $\nu_{max.}$ (Nujol) 1650, 1720, and 1750 cm.$^{-1}$.

A solution of the above ester (0·05 g.) in 2N-ammonium hydroxide (2 c.c.) after 30 hr. at 0° was shown by paper chromatography to contain a substance tentatively identified as 6-*O*-caffeoylarbutin, R_F(A) 0·42, R_F(B) 0·60. The same product resulted from hydrolysis at 100° for 3 hr. with N-hydrochloric acid.

O-*Acetylquinol* 3,4,6-*Tri*-O-*acetyl*-β-D-*glucoside*.—A solution of 3,4,6-tri-*O*-acetyl-α-D-glucosyl chloride[9] (4·0 g.), mono-*O*-acetylquinol (2·2 g.) in ether (100 c.c.) containing silver oxide (5 g.) was stirred under reflux for 4 days, fresh silver oxide (5 g.) being added after 2 days. The yellow solution was filtered free from silver salts, and evaporated to a gum which was chromatographed over alumina (50 g.) using ether as eluant. Fractions (20 c.c.) were collected, evaporated to a smaller bulk (5 c.c.), and allowed to stand at 0°. The O-*acetylquinol* 3,4,6-*tri*-O-*acetyl*-β-D-*glucoside* (0·25 g.) which separated from the first fractions was recrystallised from acetone–ether, to give fine white needles, m. p. 162—163° (Found: C, 54·2; H, 5·4. $C_{20}H_{24}O_{11}$ requires C, 54·6; H, 5·5%), $\nu_{max.}$ (Nujol) 1745 and 3500 cm.$^{-1}$.

Acetylation of the product in pyridine with acetic anhydride gave arbutin penta-acetate, m. p. and mixed m. p. 145°. Benzoylation gave a *monobenzoate*, needles (from ethanol), m. p. 135—136° (Found: C, 59·1; H, 5·3. $C_{27}H_{28}O_{12}$ requires C, 59·5; H, 5·1%). Methylation of the glucoside (0·1 g., methyl iodide, silver oxide, 2 days) gave a gum which was dissolved in acetone (10 c.c.), 5N-hydrochloric acid (5 c.c.) was added, and the solution refluxed for 3 hr. before passage down a short column of Amberlite C.G. 400 (OAc form). Concentration of the eluate gave a gum (0·02 g.) which was subjected to paper electrophoresis in germanate buffer.[10] The results are described on p. 5651.

O-*Acetylquinol* 2-O-(3,4-*Diacetoxycinnamoyl*)-3,4,6-*tri*-O-*acetyl*-β-D-*glucoside*.—(*a*) A solution of the above glucoside (0·1 g.), and 3,4-diacetoxycinnamoyl chloride (0·5 g.) in benzene (2·5 c.c.) and chloroform (2·5 c.c.) and containing pyridine (0·1 c.c.) was set aside at room temperature for 4 days and poured into ethyl acetate (25 c.c.). The solution was extracted with 2N-hydrochloric acid, saturated sodium hydrogen carbonate solution (25 c.c.), and water (25 c.c.). Removal of the solvent gave a gum which was dissolved in acetone (20 c.c.) and filtered through alumina (10 g.). Evaporation of the acetone eluate gave a further gum which was dissolved in ethanol (5 c.c.); water (5 c.c.) was added and the solution left at room temperature for ½ hr. The solution was filtered, kept at 0° for 24 hr., and the *acetate* which separated recrystallised from ethanol, to give needles (0·05 g.), m. p. 145° (Found: C, 57·2; H, 5·2. $C_{33}H_{34}O_{16}$ requires C, 57·6; H, 4·9%), $\nu_{max.}$ (Nujol) 1640, 1720, and 1760 cm.$^{-1}$.

(*b*) A solution of compound 4 (0·05 g.) in acetic anhydride (2 c.c.) and pyridine (1 c.c.) was kept at room temperature for 24 hr. before pouring into water (15 c.c.). The precipitated acetate ester formed needles (0·05 g.), m. p. 145° (from ethanol) (Found: C, 57·4; H, 5·1. Calc. for $C_{33}H_{34}O_{16}$: C, 57·6; H, 4·9%), $\nu_{max.}$ (Nujol) 1640, 1720, and 1760 cm.$^{-1}$.

The authors thank Professor R. D. Haworth, F.R.S., for his advice and interest in this work, and the D.S.I.R. for maintenance grants (M. O. N. and G. B.).

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[*Received, September 15th*, 1964.]