when no separation occurred. All 3 anthocyanins thus have the same aglycone and are cyanidin glycosides.

The sugar components were identified by a method used for the identification of the sugar components of cocoa anthocyanins[9]. Each methanolic eluate of the individual anthocyanins from Whatman No. 3 paper was evaporated to dryness in vacuo. The anthocyanins were hydrolysed for 30 min in 0.5 *N* sulphuric acid in a boiling water bath. The hydrolysates were neutralized with $BaCO_3$, centrifuged and concentrated in vacuo. The residue was extracted with methanol and the extract concentrated in vacuo to approximately 0.2 ml. The sugar chromatograms were developed in ethyl acetate-pyridin-water (2:2:1 v/v)[10], the sugar spots detected by spraying with aniline-phthalate reagent[11], and compared with standard sugars.

Table II. Rf values of the principal cyanidin glycosides and of *D. alata* anthocyanin in different solvent systems

Cyanidin glycoside	ACOH-HCl-W 5:1:5	ACOH-HCl-W 82:15:3	BAW 4:1:5	HCl-W 3:97
3-glucoside	0.61	0.26	0.38	0.07
3-galactoside	0.61	0.26	0.37	0.07
3-rhamnoglucoside	–	0.43	0.37	0.19
3-gentiobioside	–	–	0.29	–
3-xyloglucoside	0.85	0.51	0.36	0.24
3-diglucoside	–	0.61	0.33	0.34
3,5-diglucoside	0.70	0.40	0.28	0.16
3-rhamnoglucosido-glucoside	–	0.59	0.25	0.36
Major anthocyanin of *D.* alata	0.69	0.38	0.28	0.14

The sugars obtained from the major anthocyanin and from one of the minor anthocyanins could not be separated from glucose. The concentration of the third was so low that it was not possible to determine the sugar component with the amount of sample available. On the chromatograms a trace of arabinose was detected but this may be an artefact formed during the chromatography[12].

The Rf values of the anthocyanins isolated were compared with those of known cyanidin glycosides (Table II). The major component of the pigment is thus shown to be cyanidin-3-5-diglucoside.

The Rf values of the 2 minor anthocyanins when run in non-alcoholic solvents were similar to the Rf values of cyanidin-3-monoglucoside and cyanidin-3-rhamnoglucoside, but when run in BAW the Rf values did not coincide. Further studies on the 2 minor yam pigments are therefore necessary.

Résumé. Trois anthocyanines ont été extraits de tubercules d'une variété de l'igname *D. alata* à chair pourpre. Tous les 3 sont des glycosides de la cyanidine: le pigment principal est le cyanidine-3, 5-diglucoside.

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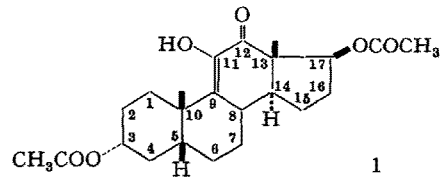
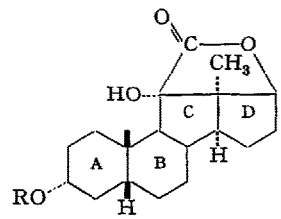
The Molecular Structure of the Benzilic Acid Rearrangement Product of 3α,17β-Diacetoxy-11-hydroxy-12-oxo-5β-androst-9(11)-ene

3α,17β-Diacetoxy-11-hydroxy-12-oxo-5β-androst-9(11)-ene (1), on treatment with base, gives a compound $C_{19}H_{28}O_4$, which can be shown to contain 2 hydroxyl groups and a lactone ring[1]. A benzilic acid rearrangement of 1, followed by lactonization between the carboxyl group at C-11 and the hydroxyl at C-17 would be stereochemically impossible with a *trans* C/D ring junction. Accordingly, a retroaldol equilibrium with epimerization at C-13 leading to a *cis* C/D ring junction prior to the benzilic acid rearrangement was postulated, and structure 2a was put forward for the lactone[1]. In this remarkable transformation numerous keto-enol equilibria could lead to a change of stereochemistry of the B/C as well as the C/D ring junctions. A crystal structure analysis was carried out on a *p*-bromobenzoyl ester of the rearrangement product to determine the stereochemistry at the B/C ring junction, postulated to be that of the naturally occurring androstanes, and to confirm the unusual structure containing three 5-membered rings all *cis*-fused[1].



1



2a R = H
b R = *p*-BrC_6H_4CO

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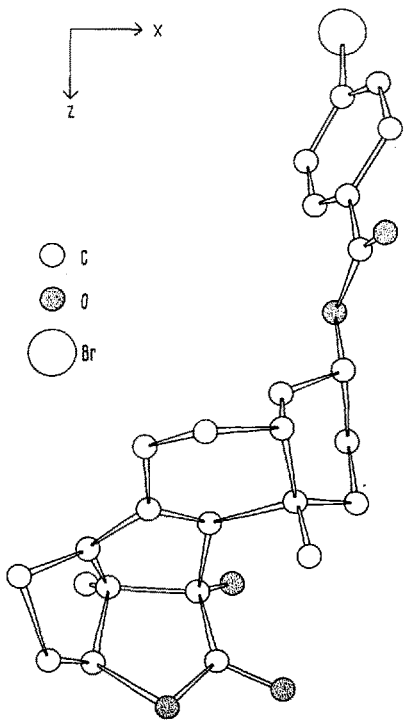
The *p*-bromobenzoyl ester ($C_{28}H_{31}O_5Br$) crystallizes as colorless needles belonging to the orthorhombic system. Cell parameters, as determined by precession methods (Mo $K\alpha$, $\lambda = 0.7107$ Å), are $a = 16.76$; $b = 7.05$, and $c = 19.58$ Å. The calculated density, assuming 4 molecules in the unit cell, is 1.44 g cm^{-3}; the measured value is 1.42 g cm^{-3}. Systematic absences indicate that the space group is $P2_12_12_1$. The data were estimated visually from equi-inclination Weissenberg photographs (Cu $K\alpha$ radiation). A total of 1493 independent structure amplitudes was recorded. The structure analysis followed the usual heavy atom procedure[2], and the positions of all the atoms were located by Fourier methods. At the present stage of refinement, the crystallographic *R*-factor on 1493 reflections is 0.11.



A view of the structure looking down the *b*-axis.

A drawing of the molecular structure viewed down the *b*-axis is shown in the Figure. The structure 2b is established for the *p*-bromobenzoate of the rearrangement product, with the B/C ring junction shown to be *trans*, and with the C_8 hydrogen atom β and the C_9 hydrogen α. The 3 five-membered rings are shown to be *cis*-fused as proposed[1,3]. Further details of the geometry of this unusual structural feature will be published at a later date[4].

Zusammenfassung. Die Struktur des *p*-Brombenzoates des Benzilsäureumlagerungsproduktes von 3α, 17β-Diacetoxy-11-hydroxy-12-oxo-5β-Δ9(11)-androsten wurde durch dreidimensionale Röntgenstrukturanalyse eines Einkristalls als 3-*p*-Brombenzoat des 11β-Carboxy-3α, 11α, 17β-trihydroxy-13α-C-nor-5β-androstan 11a, 17-Laktons erkannt.

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[3] All *cis*-fused systems have been proposed for an anhydroplatynecine, R. Adams and N. J. Leonard, J. Am. chem. Soc. *66*, 257 (1944), and for triquinacene, R. B. Woodward, T. Fukunaga and R. C. Kelly, J. Am. chem. Soc. *86*, 3162 (1964).

[4] A crystalline sample of the compound used in this analysis was kindly supplied by Dr. P. Kurath of Abbott Laboratories, North Chicago (Illinois 60064, USA). We wish to acknowledge helpful discussions with Professor P. Beak and to thank Miss Linda Kubina who carried out the data estimation used in this analysis.

A New Synthesis of Dehydromunduserone

The total synthesis of munduserone (I) was achieved from dehydromunduserone (II) by Ollis et al.[1]. Compound (II) was obtained through Hoesch procedure, followed by cyclization, from methyl (2-cyanomethyl-4,5-dimethoxyphenoxy) acetate. The preparation of the ester, however, was troublesome and did not give satisfactory results. The present paper describes a new synthetic method of (II) from 7,2′,4′,5′-tetramethoxyisoflavone (III)[2], itself a readily available substance, via tephrosic acid monomethyl ether (IV).

The reaction of 2-hydroxy-4-methoxyphenyl 2,4,5-trimethoxybenzyl ketone (V)[2] with ethyl orthoformate in pyridine-piperidine afforded (III) (m.p. 190–191°) (lit.[2], m.p. 190–191°) in 80% yield. Selective demethylation at the 2′-position of (III) in acetonitrile with anhydrous aluminium chloride furnished 2′-hydroxy-7,4′,5′-trimethoxyisoflavone (VI, m.p. 200–201°; IR 1614 cm^{-1} (C = O) (Nujol), UV λ_{max}^{EtOH} nm (log ε); 266 (4.23), 300 (4.27). Found: C, 65.85; H, 5.04. $C_{18}H_{16}O_6$ requires: C, 65.85; H, 4.91%) in 85% yield. Reaction of the isoflavone (VI) with ethyl bromoacetate in the presence of potassium carbonate gave the 2′-phenoxyacetate derivative (VII, m.p. 163–164°, IR 1736, 1647, 1633 cm^{-1} (C = O) (Nujol), UV λ_{max}^{EtOH} nm (log ε); 247.5 (4.36), 296 (4.25). Found: C, 63.69; H, 5.39. $C_{22}H_{22}O_8$ requires: C, 63.76; H, 5.35%) in 94% yield. The treatment of (VII) with dilute alkali gave tephrosic acid monomethyl ether (IV, m.p. 205–206°, IR 3250 (broad) (OH), 1735, 1635 cm^{-1} (C = O) (Nujol), UV λ_{max}^{EtOH} nm (log ε); 277 (4.21), 315 (3.94). Found: C, 60.45; H, 5.38. $C_{19}H_{20}O_8$ requires: C, 60.63; H, 5.36%) (lit.[3], m.p. 204–205°) in 71% yield. By intramolecular cyclization with acetic anhydride and anhydrous sodium

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