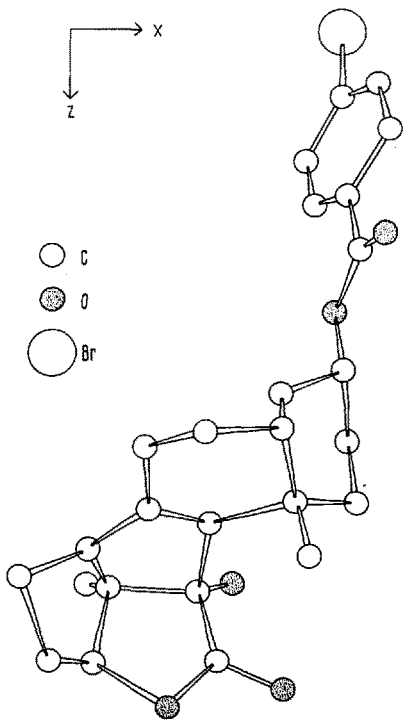
The *p*-bromobenzoyl ester ($C_{28}H_{31}O_5Br$) crystallizes as colorless needles belonging to the orthorhombic system. Cell parameters, as determined by precession methods (Mo $K\alpha$, $\lambda = 0.7107$ Å), are $a = 16.76$; $b = 7.05$, and $c = 19.58$ Å. The calculated density, assuming 4 molecules 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.

J. S. McKechnie and I. C. Paul

W. A. Noyes Chemical Laboratory, University of Illinois, Urbana (Illinois 61801, USA), 28th March 1967.

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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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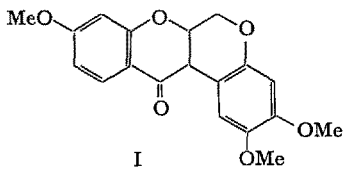
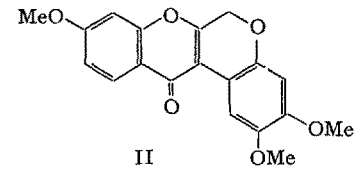
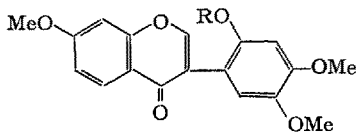


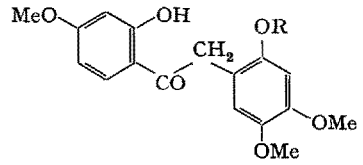
I



II



III R = Me
VI R = H
VII R = $CH_2CO_2C_2H_5$



IV R = CH_2CO_2H
V R = Me

acetate, the ether (IV) gave dehydromunduserone (II, m.p. 209–210°, IR 1634 cm^{-1} (C = O) (Nujol), UV λ_{max}^{EtOH} nm (log ε); 231 (4.48), 277 (4.39), 302 (4.23). Found: C, 67.06; H, 4.69. $C_{19}H_{16}O_6$ requires: C, 67.05; H, 4.75%) (lit. [3], m.p. 210°).

The conversion of (II) into (±)-(I) has already been reported[1], this paper, therefore, completes a new synthesis of (I).

Zusammenfassung. Eine einfache Synthese von Dehydromunduseron aus 7,2′,4′,5′-Tetramethoxy-isoflavon wird beschrieben.

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Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima (Japan), 13th March 1967.

Enhancement of Fluorescence Emission of Acridine Orange by Nucleosides

Acridine orange (AO) is one of the basic dyes exhibiting a typical binding to polynucleotides[1–7]. When AO is bound to polynucleotides, 2 types of complexes, Complex I and Complex II, are formed, depending on the concentration ratio of polynucleotide to dye. The formation of Complex I at low concentration ratio of polynucleotide to dye brings about a new absorption band at the shorter wave-length region than the absorption peak of AO monomer and the quenching of AO fluorescence. On the other hand, the formation of Complex II at high concentration ratio of polynucleotide to dye yields a red shift of absorption band of AO and the enhancement of AO fluorescence. The former complex is considered to be formed by the metachromatical binding of AO to the phosphates of polynucleotide and the latter by the intercalation of AO between base pairs.

The present article deals with the absorption and fluorescence characteristics of AO in the presence of various nucleosides to find the elementary information about the interaction between AO and nucleic acid bases. In the aqueous solution, AO has a strong tendency to form a non-fluorescent dimer in which the transition moments of monomers are parallel to each other and perpendicular to the direction of a line connecting their centres of gravity[8,9]. Therefore, the absorption spectrum of aqueous AO solution generally consists of not only the monomer $0 \rightarrow 0$ absorption band (at 492 nm) but the dimer absorption band (at 464 nm), except for in the extremely low concentrations. The dimer absorption band overlaps upon the monomer $0 \rightarrow 1$ absorption band. The absorption feature is shown in Figure 1, curve (a), where the concentration and temperature are respectively $2.10^{-5}M$ and 6 °C.

On the addition of high concentration of adenosine, the absorption spectrum undergoes pronounced changes, as shown in Figure 1, curve (1). The dimer dissociates into monomers and the monomer absorption band shifts to longer wave-lengths by about 5nm. This absorption behaviour is quite similar to that of AO when the high concentration of DNA is added to the aqueous AO solution. The absorption spectrum has a band maximum at about 502 nm at the herring sperm DNA to AO ratio of 100:1 (Complex II), as shown in Figure 1, curve (1′). Since the fluorescence-excitation spectrum coincides exactly with the absorption spectrum, curve (1′) is known to be attributable to the AO monomer complexing with DNA. The dimer originally present dissociates completely into monomers by the addition of large excess of DNA. When AO solutions in the absence and presence of adenosine or DNA are warmed up to 70 °C, the absorption spectrum changes to the free monomer band in all cases. This is shown in Figure 1, curves (b), (2) and (2′). The broadness of curve (2′) indicates that, in the case of Complex II, some fraction of AO still remains bound as Complex II even at this temperature.

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