75%); bp 53–54° (0.65 mm) and 43–44° (0.13 mm); ν_{max} ($CHCl_3$) 1725, 1445, 1375, 1265, 1160 cm^{-1}; nmr (CCl_4), 3.63 (3 H, singlet), 2.48 (4 H, multiplet), 1.43 (9 H, singlet).

Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.47; H, 8.62.

t-Butyl Hydrogen Succinate.—Methyl *t*-butyl succinate (94 g, 0.5 mole) was dissolved in 1150 ml of dioxane and an aqueous sodium hydroxide solution (20 g, 0.5 mole in 1100 ml of water) was added. The resulting clear solution was stirred for 40 hr at room temperature and then concentrated *in vacuo* until entirely aqueous. This barely alkaline solution was extracted with ether once, poured over ice, acidified with cold 2 *N* sulfuric acid (0°), and extracted six times with ether. The ethereal solution was washed with water and dried over sodium sulfate, and the solvent was removed *in vacuo*. The resulting solid was recrystallized once from petroleum ether (bp 30–60°) giving crystals: yield, 57.4 g (0.33 mole, 66%); mp 49–52° (lit.[10] mp 51.5–52°).

Diethyl 3-Carbo-t-butoxypropionylmalonate (6).—Diethyl ethoxymagnesiomalonate was prepared according to Price and Tarbell[12] by adding 0.5 ml of carbon tetrachloride, 5 ml of absolute ethanol, and 6 ml of a mixture of diethyl malonate (24 g, 0.15 mole) and ethanol (11 ml) to a flask containing 3.7 g (0.15 g-atom) of magnesium turnings. The vigorous reaction was moderated by cooling before dropwise addition of the remainder of the mixture. After complete addition, 60 ml of anhydrous ether was added and the flask contents were warmed to reflux for several hours until almost all the magnesium was consumed. All volatile material was removed *in vacuo* and replaced with benzene. The benzene was also distilled *in vacuo* and the solid residue was dissolved in 60 ml of anhydrous ether for addition to the mixed anhydride prepared simultaneously.

The mixed anhydride was prepared by the dropwise addition of ethyl chloroformate (16.3 g, 0.15 mole) to a stirred solution containing *t*-butyl hydrogen succinate (26.5 g, 0.15 mole), triethylamine (15.2 g, 0.15 mole), and anhydrous toluene (150 ml). The reaction flask was cooled in an ice–salt slurry and its contents were maintained just below 0°. After this addition was complete, the flask contents were stirred for 30 min prior to the addition of the diethyl ethoxymagnesiomalonate. The flask remained in the ice–salt slurry and the addition was again slow enough to maintain the contents below 0°. After addition, the reaction was stirred overnight at room temperature. The flask contents were poured over ice and acidified cautiously with cold 2 *N* sulfuric acid (0°). The mixture was shaken in a separatory funnel until clear and the solution was ascertained to be acidic before extracting twice with ether. The combined organic solutions were washed twice with cold 2 *N* sulfuric acid (0°), with sodium bicarbonate solution, and then with water until the washings were neutral. After drying over sodium sulfate, the solvents were removed *in vacuo*, leaving a liquid residue (positive ferric chloride test). The residue was distilled and a colorless, viscous liquid resulted: yield, 30 g (0.095 mole, 63%); bp 112–113° (0.03 mm); ν_{max} ($CHCl_3$) 1760, 1725, 1648, 1615, 1372, 1245, 1152, 1090, 1029 cm^{-1}; nmr ($CDCl_3$), 14.03 (1/3 H, singlet), 4.55 (2/3 H, singlet), 4.23 (4 H, quartet), 2.73 (4 H, multiplet), 1.45 (singlet), 1.30 (triplet) (bands at 1.45 and 1.30 represent 15 H; when shaken with D_2O, the 14.03 band disappeared; on addition of sodium carbonate, the 4.55 band also disappeared).

Anal. Calcd for $C_{15}H_{24}O_7$: C, 56.95; H, 7.65. Found: C, 57.21; H, 7.53.

2-Carbethoxy-4-carbo-t-butoxycyclopentane-1,3-dione (7).—In a 500-ml, three-necked, round-bottom flask, equipped with dropping funnel, mechanical stirrer, and reflux condenser fitted with drying tude, were placed 200 ml of anhydrous benzene, 30 ml of anhydrous *t*-butyl alcohol, and 6.0 g (0.15 g-atom) of potassium metal. The potassium was allowed to react using no external heat and when the reaction was complete, the slurry was brought to gentle reflux by means of an oil bath heated to 95–100°. To this off-white slurry was added a solution of 15.8 g (0.05 mole) of diethyl 3-carbo-*t*-butoxypropionylmalonate in 50 ml of benzene, over a period of 30 min. After addition was complete, the mixture was allowed to reflux for an additional 1.75 hr and then allowed to stir at room temperature overnight. The reaction flask contents were poured over crushed ice and acidified with cold 2 *N* sulfuric acid (0°). The mixture was shaken with ethyl acetate in a separatory funnel. The aqueous solution was ascertained to be acidic, separated, saturated with sodium chloride, and extracted with three 200-ml portions of ethyl acetate. The combined ethyl acetate solutions were extracted with saturated aqueous sodium bicarbonate solution, using four 200-ml portions. The aqueous extracts were washed once with benzene, poured over crushed ice, and carefully acidified with cold 2 *N* sulfuric acid (0°) before saturating with sodium chloride and extracting with four 300-ml portions of ethyl acetate. The ethyl acetate solutions were combined and washed with saturated sodium chloride solution until the washings showed a pH increase. The solution was dried and the solvent was removed *in vacuo* leaving an orange oil which crystallized on standing (11.8 g, 0.044 mole, 87% crude yield). An earlier cyclization using the same conditions had produced a similar product (11.4 g, 0.042 mole, 84% crude yield) of comparable purity (tlc, silica gel G developed with 5% methanol in chloroform). The crude product (11.8 g) was recrystallized from warm benzene by adding petroleum ether and cooling this solution to 0° for 2 days. Much of the material had to be recrystallized twice to free it from an oily impurity. The white, crystalline beads obtained had mp 81–84°: yield, 7.3 g (54%). A small sample was recrystallized further in the same manner and the white solid resulting had mp 84–85°; ν_{max} ($CHCl_3$), 3300–2700 (broad), 1714, 1660, 1610, 1474, 1437, 1385, 1377, 1340, 1230, 1160, 1052; λ_{max} (0.1 *N* HCl) 248 mμ (ε 21,000); λ_{max} (0.1 *N* NaOH) 250 mμ (ε 27,000); nmr ($CDCl_3$), 11.67 (1 H, broad), 4.53 (2 H, quartet), 3.70 (1 H, four lines), 3.04 (2 H, unresolved multiplet), 1.53 (singlet), 1.43 (two lines of triplet, third line under 1.53 band), bands at 1.53 and 1.43 represent a total of 12 H.

Anal. Calcd for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71. Found: C, 57.95; H, 6.75.

2-Carbethoxycyclopentane-1,3-dione (12).—The cyclic diketo diester **7** (2.70 g, 0.01 mole) was dissolved in 200 ml of anhydrous benzene along with 0.4 g of fused *p*-toluenesulfonic acid and the suspension was heated at reflux in an oil bath for 10 hr. The solid obtained after filtration and solvent evaporation was sublimed at 0.05 mm and 55°. The white sublimate (1.04 g, 61%) had mp 95–96°. A small amount of this material was purified further by tlc on silica gel plates (Mallinckrodt TLC-7) developed with 5% ethanol in ethyl acetate, followed by resublimation. The white solid resulting had mp 104°; λ_{max} (0.1 *N* HCl) 243 mμ (ε 22,200); λ_{max} (0.1 *N* NaOH) 252 mμ (ε 29,800); nmr ($CDCl_3$), 11.2 (1 H, singlet), 4.42 (2 H, quartet), 2.65 (4 H, singlet), 1.37 (3 H, triplet); infrared absorptions ($CHCl_3$) 1714, 1656, and 1609 cm^{-1}.

Anal. Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.93. Found: C, 56.65; H, 6.07.

Cyclopentane-1,3-dione (13). A. From 2-Carbethoxy-4-carbo-t-butoxycyclopentane-1,3-dione (7).—A solution of **7** (270 mg, 1 mmole) in 60 ml of 6 *N* hydrochloric acid was heated on a steam cone for 5 hr. The solid obtained after solvent evaporation was sublimed at 0.5 mm and 100° to give white crystals: yield, 49 mg (50%); mp 150–151° (lit.[6] mp 151–152°). Identity was confirmed by comparison of infrared spectra.

B. From 2-Carbethoxycyclopentane-1,3-dione (12).—A solution of **12** was hydrolyzed and worked up as above. The white sublimate had mp 151–152°, yield 65 mg (73%).

Registry No.—**7**, 14734-23-7; **12** enol, 14734-24-8; methyl *t*-butyl succinate, 14734-25-9.

Acknowledgment.—We are indebted to the National Cancer Institute for financial support.

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A New Isoflavone Glycoside from *Baptisia australis*

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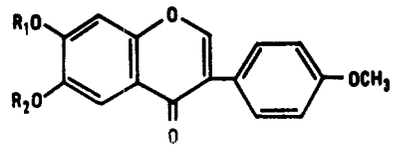
We wish to report the isolation and structure determination of a new isoflavone glycoside which belongs

to the rare group of 6,7-dioxygenated isoflavones. The glycoside, which we named texasin 7-O-β-D-glucoside, is the major isoflavone in *Baptisia australis* (Leguminosae). The aglycone texasin, also a minor isoflavonoid constituent of the species, is shown to be identical with synthetic 6,7-dihydroxy-4′-methoxyisoflavone. Isoflavones previously reported[1] from *B. australis* include formononetin, formononetin 7-O-β-D-glucoside, afrormosin (I), and afrormosin 7-O-β-D-glucoside.



I, R_1 = H; R_2 = CH_3
II, R_1 = glucose; R_2 = H
III, R_1 = H; R_2 = H

Texasin 7-O-glucoside (II), $C_{22}H_{22}O_{10}$, was isolated in 0.2% yield from a methanol extract of *B. australis* leaf and stem material. The ultraviolet spectrum (λ_{max} 225 shoulder, 258, 325 nm), although flavonelike, resembled that of afrormosin (λ_{max} 226, 254, 326 nm), the well-pronounced long-wavelength band of which appears to be characteristic in isoflavones of 6,7 dioxygenation.[2,3]

The pmr spectrum of trimethylsilylated texasin glucoside shows a typical[1,4] isoflavone C-2 proton singlet at 7.84 ppm (*cf.* C-3 proton in flavones, 6.2–6.4 ppm), thereby confirming the isoflavonoid nature of II. A 6,7-dioxygenated A ring is indicated by the presence of singlet H-5 and H-8 signals at 7.63 and 6.93 ppm, respectively, and a 4′-monooxygenated B ring is evidenced by the pair of two-proton doublets (J = 9 cps) at 7.45 and 6.89 ppm (*cf.* formononetin 7-O-glucoside: 7.46, 6.86 ppm[1]). A single methoxyl signal is present at 3.78 ppm, a value well within the range established[4] for isoflavone 4′-methoxyl groups, and this, considered together with the virtual identity of the B-ring proton signals in II and in formononetin 7-glucoside, suggests that the methoxyl group is at the 4′ position.

Acid hydrolysis of II produced the aglycone texasin, III (also occurring in the plant), which was shown to possess an *o*-dihydroxyl group in the A ring by ultraviolet spectroscopy. Added $AlCl_3$ produced a 20-nm shift in the long-wavelength band and NaOAc–H_3BO_3 produced a 9-nm shift which, in the absence of both a 5-hydroxyl group and a B-ring *o*-dihydroxyl group is taken to indicate a free *o*-dihydroxyl group in the A ring. This evidence suggests that texasin is 6,7-dihydroxy-4′-methoxyisoflavone (III) and direct comparison with synthetic material[5] confirmed the identity.

The single sugar in II, indicated by the pmr spectrum, was shown to be glucose by paper chromatography and by hydrolysis with β-glucosidase. A β linkage to the aglycone is suggested both by the enzymatic hydrolysis and by the glucose H-1 pmr signal which has a coupling constant of 7 cps.[6] Of the two possible positions for the sugar attachment, the 7-hydroxyl group was favored since on 2D paper chromatography the texasin glucoside spot is found adjacent to both formononetin 7-glucoside and afrormosin 7-glucoside. It is not possible, however, to distinguish between the 6- and 7-O-glucoside possibilities by ultraviolet spectroscopy since the 7-hydroxyl group in flavonoids is known to give poor shifts with NaOAc when either a 6- or 8-oxygen substituent is present in the same molecule.[7] The method used, therefore, was to methylate texasin glucoside completely prior to hydrolysis. The compound produced by acid hydrolysis of this derivative proved to be spectrally and chromatographically identical with afrormosin (I), thereby proving that the glucose unit is attached at the 7-hydroxyl group. Texasin glucoside is therefore assigned structure II.

Only one isoflavone with the unusual 6,7,4′-oxygenation pattern, afrormosin, has previously been reported as a natural product,[8] although 6,7,4′-trihydroxyisoflavone may occur in the soya bean *Glycine soja*.[9] Both of these compounds occur within the subfamily Papilionoideae of the Leguminosae, afrormosin having been found in the tribes Sophoreae,[8] Galageae,[8] and Podalyrieae.[10] The current isolation of texasin and its 7-O-glucoside from a member of the tribe Podalyrieae together with afrormosin is consistent with this chemotaxonomic pattern. Preliminary paper chromatographic analysis of a number of *Baptisia* species indicates that both afrormosin and texasin derivatives may also occur in other members of this genus.

Experimental Section

Melting points are uncorrected. Solvent systems used in paper chromatography are abbreviated as follows: *t*-BuOH–HOAc–H_2O, 3:1:1 (TBA); 15% acetic acid (HOAc); and the benzene layer of a mixture of benzene–HOAc–H_2O, 6:7:3 (Bz).

Texasin 7-O-β-D-Glucoside (II).—Finely ground *B. australis*[11] leaf and stem material (21.6 g) was extracted with boiling 25% aqueous methanol for 1.5 hr. The extract (3.2 g) was dissolved in methanol and chromatographed on a polyamide column using water containing increasing amounts of methanol as eluent. The fractions eluted with 60% methanol gave crystals of texasin glucoside (0.04 g) on evaporation. Repeated crystallization of this material from aqueous methanol gave white crystals: mp 204–206°; λ_{max} (CH_3OH) 225 shoulder, 258, 325 nm (log ε 4.27, 4.53, 3.96); λ_{max} ($NaOCH_3$) 253, 367 nm; λ_{max} (NaOAc) 256, 325, 370 shoulder nm; λ_{max} ($AlCl_3$) as for methanol; R_f values, 0.56 (TBA), 0.66 (HOAc); *cf.* formononetin 7-glucoside, 0.65, 0.77, and afrormosin 7-glucoside, 0.62, 0.75, in the same solvents, respectively. The pmr spectrum of trimethylsilylated II[12] exhibited signals at 7.84 (singlet, H-2), 7.63 (singlet, H-5), 7.45 (doublet, J = 9 cps, H-2′, -6′), 6.93 (singlet, H-8), 6.89 (doublet, J = 9 cps, H-3′, -5′), 5.03 (doublet, J = 7 cps, glucose H-1), 3.78 (singlet, 4′ OCH_3), and 3.1–3.8 ppm (broad, six glucose protons).

Anal. Calcd for $C_{22}H_{22}O_{10}$: C, 59.19; H, 4.97. Found: C, 59.03; H, 5.12.

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(5) We are indebted to Dr. M. Sainsbury of Bath University of Technology for the sample of 6,7-dihydroxy-4,-methoxyisoflavone. For the synthesis, see ref 2.

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Texasin (III).—Hydrolysis of II with 5% HCl for 1 hr at 100° gave a white precipitate which crystallized from methanol: mp 285–287° (lit.[2] mp 291.5–292.5°); λ_{max} (CH_3OH) 227 shoulder, 254, 324 nm; λ_{max} ($NaOCH_3$) 252, 350 nm; λ_{max} (NaOAc), 251, 346 nm; λ_{max} (NaOAc–H_3BO_3) 250 shoulder, 333 nm; λ_{max} ($AlCl_3$)2 15, 232 shoulder, 250, 344 nm; λ_{max} ($AlCl_3$–HCl) 227 shoulder, 254, 322 nm; R_f values, 0.80 (TBA), 0.31 (HOAc), 0.4 (Bz); *cf.* formononetin, 0.87, 0.40, 0.6, and afrormosin, 0.85, 0.35, 0.9, in the same solvents, respectively.

Texasin was also isolated by paper chromatography of the crude *B. australis* methanol extract and by β-glucosidase hydrolysis of the glucoside in distilled water at 25°.

Sugar Analysis of Texasin 7-O-Glucoside (II).—The sugar–aglycone mixture obtained from acid hydrolysis of II was paper chromatographed using EtAc–pyridine–H_2O (12:5:4) as solvent. The sugar was detected using a *p*-anisidine hydrochloride spray reagent[10] and proved to be identical with glucose.

Synthesis of Afrormosin from Texasin 7-O-Glucoside (II).—Texasin 7-glucoside (4 mg) in methanol (2 ml) was treated with an ether solution of CH_2N_2 until an ultraviolet spectrum of the resultant solution showed no change on the addition of $NaOCH_3$. Acid hydrolysis of the product gave the methylated aglycone which was chromatograpically (TBA, HOAc, and Bz systems) and spectrally identical with afrormosin.

Registry No.—III, 897-46-1.

Acknowledgments.—This work was supported by the National Institutes of Health (Grant GM-11111-04A1), the National Science Foundation (Grant GB 5448X), and the Robert A. Welch Foundation (Grant F-130).

Photodimerization. I. The *syn* and *anti* Photodimers of 1,4-Naphthoquinone

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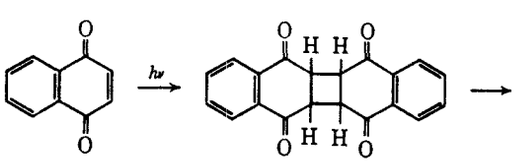
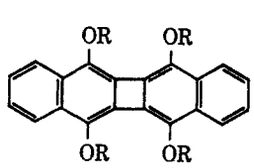
Schönberg, Mustafa, *et al.*,[1] reported, in 1948, the photolytic dimerization of 1,4-naphthoquinone (I) to II (mp 244–248°). Bruce[2] succeeded in converting II into the 2,3-binaphthylene derivatives III, IV, and V.



I II



III, R = H
IV, R = Me
V, R = Ac

The symmetrical nature of the 2,3 double bond in I confines the possible number of C_4 photodimers of I to two, namely the *anti* dimer (IIa) and the *syn* dimer (IIb). Compound IIb will be by far the more strained

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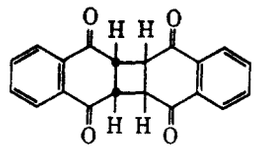
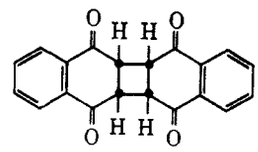


IIa



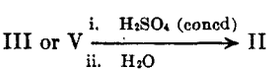
IIb

owing to its rather unsymmetrical all-*cis* structure and consequent steric repulsion.

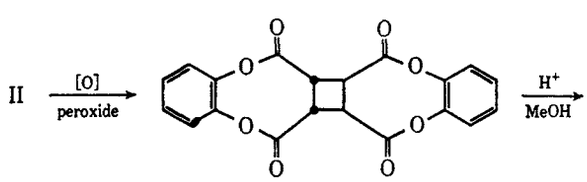
The *anti* Photodimer (IIa).—As a result of lower inherent strain in IIa compared with IIb, we expected that the *anti* dimer (IIa) will be formed preferably during photolysis of I.

The high degree of double-bond fixation of the four central π bonds in 2,3-binaphthylene[3] led us to the assumption that ketonization of III could be accomplished, leading to the thermodynamically more stable naphthoquinone dimer, namely, IIa.

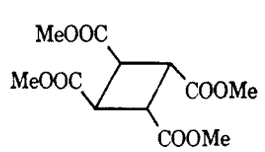
Both III and V dissolve easily in cold concentrated sulfuric acid. Subsequent dilution of the reddish solutions led to the quantitative formation of the Schönberg–Mustafa dimer (II), indicating that II must have an *anti* configuration. Proof of the *anti* configuration of II was obtained by the Baeyer–Villiger oxidation, which is known to proceed with retention of configuration,[4,5]



of II to VI. On refluxing VI in methanol containing sulfuric acid, *cis,trans,cis*-tetracarbomethoxycyclobutane (VII)[6,7] was obtained.



VI



VII

The *syn* Photodimer (IIb).—Several cases[8,9] are, however, known where both the *syn* and *anti* dimers were produced during photolysis of olefinic compounds. In the case of cyclohexadiene,[10] the *anti* dimer was shown to be the major product. The possibility that the *syn* dimer (IIb) could be formed in addition to IIa during the photolysis of I might therefore not be excluded. It was further argued that IIb, owing to its lesser degree of symmetry, should have a higher solubility than IIa. We therefore refluxed the crude photoproduct of I in methanol in which IIa is practically

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