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REDUCTION OF BRAZILEIN[a]
OCCURRENCE OF REDUCTIVE COUPLING

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Abstract—Reduction of brazilein (1) with zinc dust/acetic acid, followed by acetylation, gives a substance which has hitherto been regarded as $C_{16}H_8(OAc)_4$.[1] This has now been recognized to be the hexacetyl derivative of a bibrazilanyl formed from 2 molecules of brazilein by reductive coupling. Conclusive evidence that the compound is bi-O-triacetyl-*cis*-brazilan-4-yl (7) has been obtained. In addition, O-triacetyl-*cis*-brazilane (3) was found to be a major, and anhydro-O-triacetylbrazilin (5) a minor reaction product.

A plausible mechanism for the formation of these compounds is discussed. Full analyses of the ^1H NMR spectra of the major reaction products (3) and 7) are also presented.

At the beginning of this century Herzig and Pollak reported[1] that the reduction of brazilein (1) with zinc dust and acetic acid, followed by treatment with sodium acetate and acetic anhydride, produced a substance which, after crystallization from acetic acid, had m.p. 210–211°, and a composition consistent with the formula $C_{16}H_8(OAc)_4$.

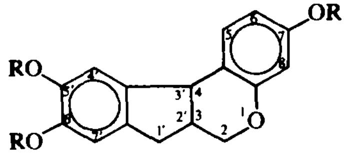
When this experiment was repeated[2] half a century later, a purer product (m.p. 227–228°) was obtained, which also gave analytical data compatible with the formula $C_{16}H_8(OAc)_4$. A remarkable feature of this compound was that simultaneous hydrolysis and methylation converted it into a substance which was regarded as a derivative of *trans*-brazilane (2, R = Me). Although this implied that the parent compound was probably O-triacetyl-*trans*-brazilane (2, R = Ac), this lead from chemical evidence was not further pursued at that time.

We have re-investigated the problem with the aid of techniques not available at the time of the previous studies,[1,2] and are now in a position to propose a structure for the alleged "tetra-acetate" on the basis of additional evidence.

The Herzig and Pollak experiment was repeated with the modifications described in the Experimental, and the crystalline compound separated as usual from the amorphous by-products, which we have also identified. Without further purification the crystalline compound melted with decomposition at 230° and, according to TLC, was entirely homogeneous; its NMR spectrum clearly showed only three acetyl groups and indicated that the remaining aliphatic protons were part of a saturated system, but there was some doubt about the accuracy of their integration. When the measurements were repeated with a sample which had been prepared for microanalysis by crystallization from acetic acid and drying in a vacuum at 110°, the spectrum exhibited an additional absorption at 7·9 τ, corresponding to the methyl protons of acetic acid, and estimated by integration to amount to approximately 0·25 mole; in all other respects the spectrum was the same as before. Monitoring by NMR while the compound was dried in a vacuum at 140° revealed that the elimination of acetic acid proceeded very slowly and was only complete after about 24 h; microanalysis then indicated a molecular formula of $C_{22}H_{20}O_7$, which could agree with a triacetylbrazilane.

The change in the acetic acid content had virtually no effect on the m.p.; the presence of 0·25 mole of this acid suffices, however, to lower the carbon content of triacetylbrazilane to the values previously reported.[1,2] This simple explanation for the misleading analytical results is undoubtedly correct, for a sample of the Herzig and Pollak compound, kindly provided by Dr. J. N. Chatterjea, and presumably identical with the material he had used in his previous investigation,[2] did in fact contain about 0·25 mole of acetic acid.

At this stage we decided to compare the spectral characteristics of the compound, m.p. 230° with those of O-triacetyl-*cis*-brazilane (3, R′ = H),[2,3] which was prepared in an unequivocal manner from triacetylbrazilin (4, R = OH),[4] as described later. The UV and IR spectra of these two compounds



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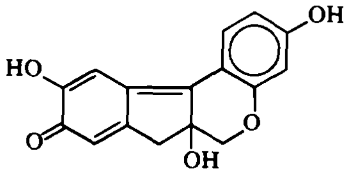
[a] The nomenclature adopted by Chatterjea, Robinson and Tomlinson[11] is used in this communication.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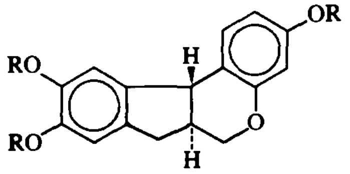
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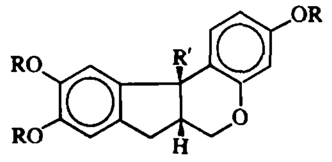
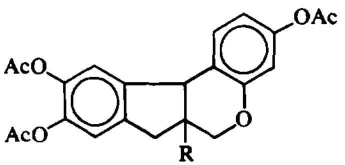

3: R = Ac, R′ = H.
7: R = Ac, R′ = *O*-triacetyl-*cis*-brazilan-4-yl
8: R = Me, R′ = *O*-trimethoxy-*cis*-brazilan-4-yl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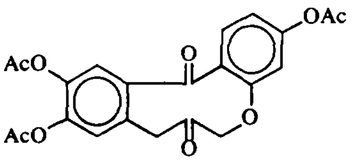
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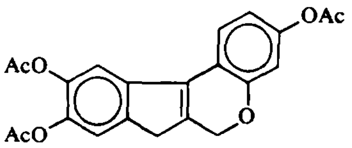
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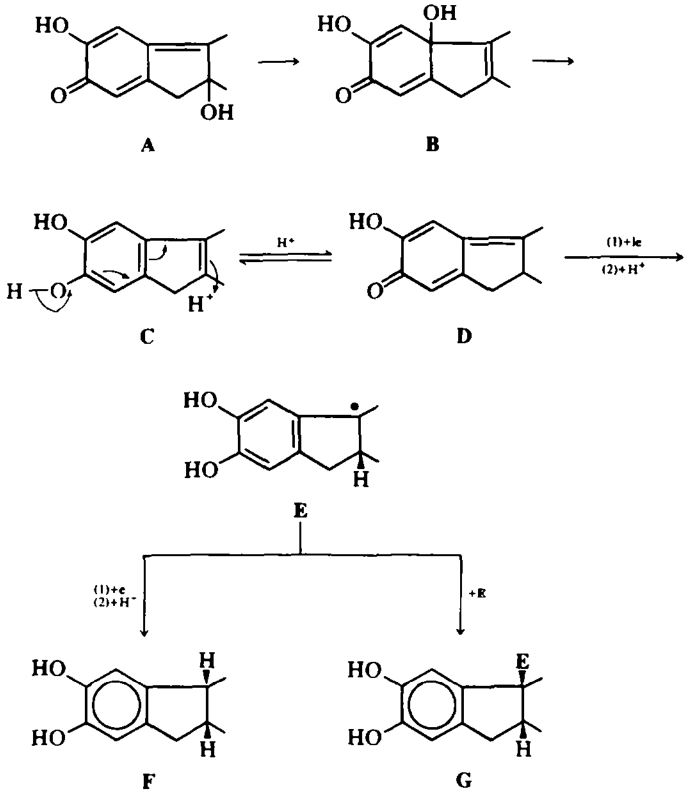
were virtually identical; their NMR spectra, on the other hand, revealed such marked differences that doubts arose about the unknown compound possessing the indenochroman ring system of brazilin. These were, however, dispelled when oxidation with chromic acid gave O-triacetylbrazilone (5),[5] which can only be obtained from a brazilin-type structure. In view of this conflicting evidence it became essential to obtain a spectrum of the compound, m.p. 230° which could be fully analyzed; this was impossible at 60 MHz, because the spin system of the relevant aliphatic protons was too tightly coupled. At 220 MHz it became evident that, relative to three acetoxyl groups, there were only 5 other aliphatic protons present, which were coupled in a $-CH_2-\overset{|}{C}H-CH_2-$ sequence. Furthermore, ^{13}C NMR showed the presence of a quaternary carbon. These results led to the conclusion that the substance is a dimeric O-triacetylbrazilanyl, originating from reductive coupling of two molecules of brazilein (1). Although the mass spectrum did not show the expected molecular ion peak at 790, it did show significant ions at *m/e* 396 and 394, resulting presumably from disproportionation of the molecule $C_{44}H_{38}O_{14}$ during volatilization. We have confirmed by NMR that this interpretation is correct: the spectrum of the compound, m.p. 230°, after decomposition by heat, showed that disproportionation into O-triacetyl-*cis*-brazilane (3) and anhydro-O-triacetylbrazilin (6) had occurred. We therefore propose that the Herzig and Pollak compound is *bi-O-triacetyl*-cis-*brazilan*-4-*yl* (7).

Using milder conditions than described before,[2] simultaneous hydrolysis and methylation of the compound (7) readily gave *bi-O-trimethyl*-cis-brazilan-4-*yl* (8), m.p. 192–4°, reported[2] m.p. 188–90°.

The amorphous, alcohol-soluble residue which remained after isolation of the bibrazilanyl (7) could only be induced to crystallize after column chromatography over silica gel. The following components were then isolated in a pure state by fractional crystallization: O-triacetyl-*cis*-brazilane (3), the corresponding bibrazilanyl (7), and anhydro-O-triacetylbrazilin (6). The NMR spectrum of the material recovered from the mother liquors showed it to be a mixture of these three compounds. Since the unsaturated compound (6) and the bibrazilanyl derivative (7) both exhibit characteristic NMR absorptions, a reasonably accurate quantitative evaluation of the spectrum was possible. The estimated values were taken into account in assessing that at 88% conversion of brazilein 55% O-triacetyl-*cis*-brazilane (3), 40% hexa-acetylbibrazilanyl (7), and 5% anhydro-O-triacetylbrazilin (6) had been formed in the reaction.

The reaction probably takes the course outlined below (part structures A–G). The first step is an acid-catalyzed allylic rearrangement which transforms brazilein (A) to the quinol (B). It is well known that compounds of this type are very readily reduced to phenols,[6] and it can therefore be assumed that under the experimental conditions the intermediate (B) is immediately reduced to anhydrobrazilin (C). In acid solution this is in equilibrium with deoxybrazilein (D), from which the radical (E) is produced by a one electron reduction and subsequent attachment of a proton to the oxygen atom. (This stage has occasionally been attributed to the formation of a radical ion, but the term has little meaning when the ion is phenoxide or alkoxide, and the medium is strongly acidic. Indeed, the exact sequence of the processes is unknown.) Further reduction then leads to *cis*-brazilane (F), while coupling of the radicals (E) produces the bibrazilanyl (G). The final step is the acetylation of the hydroxyl groups.



It is part of this hypothesis that the acetyl derivative of anhydrobrazilin (6) will not be reductively coupled to a dimeric molecule. This is fully borne out by the observation that *simultaneous* reduction and acetylation of brazilein gives exclusively anhydro-O-triacetylbrazilin (5),[2,7] which is also the main product when the reductive acetylation is carried out in the absence of acetic acid.[8]

An authentic specimen of O-triacetyl-*cis*-brazilane (3) was prepared from triacetylbrazilin (4, R = OH) by way of the tosylate (4, R = tosyl) which, on boiling with pyridine, was converted into anhydro-O-triacetylbrazilin (6); catalytic hydrogenation gave the *cis*-derivative (3). The conditions for the formation of the tosyl ester (4, R = tosyl) appear to be critical, for after a successful first experiment some difficulty was experienced before the procedure could be repeated.

DISCUSSION OF NMR SPECTRA

The 220 MHz spectrum of bi-O-triacetyl-*cis*-brazilan-4-yl (7) shows that both halves of the molecule give identical signals and therefore only one brazilanyl radical need be considered.

Apart from the signals of the aromatic and acetyl protons, the really informative part of the spectrum was a five spin system absorbing between 5·9 and 8·5 τ, the analysis of which was decisive in assigning a structure to the molecule.

The initial parameters calculated from this region of the spectrum provided values for its computer simulation by the programme MARIP.[9] Slight variations of these figures gave a good correlation between the computed and the experimental spectrum. The J-values thus obtained gave clear evidence for a $-CH_2-\overset{|}{C}H-CH_2-$ sequence; this proved that there was no proton attached to carbon − 4; the presence of a quaternary carbon atom was confirmed by ^{13}C NMR. These facts together with the elemental analysis and chemical evidence, can only be accounted for by a molecule in which 2 brazilanyl radicals are joined to each other by a bond between the carbon atoms at position – 4.

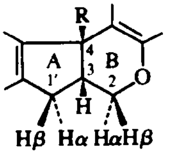
In interpreting the chemical shifts of the five relevant protons, it was reasonable to assign the absorptions at lowest field to the two protons adjacent to oxygen. The signals at 8·0 and 8·5 τ, from two geminally coupled protons, had therefore to be assigned to the benzylic group, although these are at unusually high field. This apparent anomaly can be accounted for by the dimeric nature of the compound if there is a preferred conformation of the molecule in which the benzylic protons lie over the plane of one of the aromatic rings of the other brazilanyl moiety. The assignment of the two pairs of geminal protons is entirely consistent with their J-values: the geminal coupling constant of the CH_2 next to oxygen is less negative (– 11·0 Hz) than that of the benzylic CH_2 (– 17·0 Hz), as expected from the relative effects of an adjacent electronegative atom and a π-system respectively.

The Dreiding model of the compound shows that the oxygen containing ring can exist in two half-boat conformations. The preferred form was deduced from the vicinal coupling constants of the $>$CH–CH_2–O– group by calculation of the dihedral angles from the Karplus equation.[10] The large difference between the coupling constants of H – 2α and H – 2β to H – 3, and the absolute magnitude of these values, favour the conformer where H – 2α is axial and H – 2β equatorial (relative to H – 3 being β-oriented, see structure below). In the second possible conformation H – 3 almost bisects the angle between H – 2α and H – 2β and therefore the appropriate coupling constants would have a similar value.

Analysis of the 220 MHz spectrum of O-triacetyl-*cis*-brazilane (3) showed very little difference in the analogous coupling constants, indicating that the conformation of ring B is the same as in compound (7). If, in the Dreiding model, the 5-membered ring is slightly twisted out of plane by rotation around the C–C bond common to rings A and B, the coupling constants of H – 3 to H – 1′α, H – 1′β and H – 4 are also satisfactorily accounted for.

From a comparison of the computed and experimental spectra it was evident that long-range couplings are present in both molecules, possibly of a benzylic nature as well as within the saturated system itself. Since they do not affect the general conclusions they have been omitted from the calculations.

In the Table the values and coupling constants of the relevant protons in compounds (3) and (7) are reproduced for direct comparison. The data provide strong evidence for the proposal that the bond in the bibrazilanyl (7) links the two 4-positions. The remarkable shielding of the benzylic protons ($H_{1'\alpha}$ and $H_{1'\beta}$) can also be clearly seen.



	Compound 7	*Compound 3*
$H_{2\beta}$	τ 5·91	τ 5·88
$H_{2\alpha}$	τ 6·67	τ 6·38
H_3	τ 6·88	τ 7·06
$H_{1'\alpha}$	τ 8·05	τ 7·34
$H_{1'\beta}$	τ 8·55	τ 6·80
H_4	—	τ 5·71
$J_{2\alpha 2\beta}$	– 11·0 Hz	– 11·25 Hz
$J_{2\alpha 3}$	12·5 Hz	10·0 Hz
$J_{2\beta 3}$	6·0 Hz	5·0 Hz
$J_{1'\alpha 1'\beta}$	– 17·0 Hz	– 16·5 Hz
$J_{1'\alpha 3}$	1·25 Hz	2·0 Hz
$J_{1'\beta 3}$	8·0 Hz	7·0 Hz
$J_{3\beta 4}$	—	7·0 Hz

EXPERIMENTAL

^{1}H NMR spectra were recorded with a Perkin-Elmer R 10 (60 MHz) and a Varian HR-220* instrument for solns in $CDCl_3$ containing TMS as internal reference. UV and IR spectra were determined for chloroform solns and Nujol mulls respectively. TLC was carried out on sheets of Eastman Silica Gel 6060 with benzene–ether (4:1) as solvent. Light petroleum without further specification refers to the fraction b.p. 60–80°. Organic extracts were dried with $MgSO_4$.

Reduction and acetylation of brazilein

Formation of O-*triacetyl*-cis-*brazilane* (3), *bi*-O-*triacetyl*-cis-*brazilan*-4-*yl* (7), *and anhydro*-O-*tri-acetylbrazilin* (6). The reported procedure[1] was modified as follows. A mixture of brazilein (2 g), zinc dust (8 g) and glacial AcOH (40 ml) was refluxed (oil bath) with vigorous stirring under N_2 for 3 h. Ac_2O (24 ml) and fused NaOAc (2 g) were added and refluxing and stirring continued for 4 h, when the soln had become colourless. The hot mixture was filtered and the Zn dust thereby removed was washed with AcOH. Addition of ice-cold water (250 ml) to the filtrate precipitated an amorphous yellowish solid (2·64 g) which was collected after standing overnight, and thououghly washed with water and cold EtOH.

(a) *Bi*-O-*triacetyl*-cis-*brazilan*-4-*yl* (7). A suspension of the above crude product (2·46 g) in EtOH (50 ml) was heated on the water bath until no more crystalline material was deposited; this was rapidly collected by filtration while hot, washed with hot alcohol, and finally with ether. The filtrate and washings were worked up as described under (b).

The colourless crystalline product (787 mg), m.p. 230° (dec.) was a pure compound (TLC). Samples for elemental and spectroscopic analysis were recrystallized from benzene–light petroleum and heated over phosphoric

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anhydride in a vacuum at 140° for 24 h. The compound, which was identified by NMR as *bi-O-triacetyl*-cis-*brazilan-4-yl* (7), was thus obtained as small colourless prisms, m.p. 231–2° (dec.); λ_{max} 285·5 nm (ϵ 10,560); NMR (220 MHz), τ 2·61 (1H, H-4′ or H-7′), 3·16 (1H, H-4′ or H-7′), 3·38 (1H, H-8), 3·64 (2H, H-5 and H-6), 5·91 (1H, dd, $J_{2\alpha 2\beta}$ −11·0, $J_{2\beta 3}$ 6·0 Hz, H-2β), 6·67 (1H, dd, $J_{2\alpha 2\beta}$ −11·0, $J_{2\alpha 3}$ 12·5 Hz, H-2α), 6·88 (1H, m, $J_{2\beta 3}$ 6·0, $J_{2\alpha 3}$ 12·5, $J_{31'\alpha}$ 1·25, $J_{31'\beta}$ 8·0 Hz, H-3), 7·65, 7·72 and 7·76 (9H, 3s, $3C\underline{H}_3.CO$), 8·05 (1H, bd, $J_{31'\alpha}$ 1·25, $J_{1'\alpha 1'\beta}$ −17·0 Hz, H-1′α), 8·55 (1H, dd, $J_{31'\beta}$ 8·0, $J_{1'\alpha 1'\beta}$ −17·0 Hz, H-1′β) Found: C, 67·0; H, 5·0; *m/e*, 394 and 396, $C_{44}H_{38}O_{14}$ requires: C, 66·8; H, 4·8% *M*, 790).

(b) *Work-up of the alcohol soluble part of the reaction mixture.* After removal of the dimer the combined alcoholic filtrate and washings were evaporated, the residue (1·67 g) was dissolved in benzene and chromatographed over freshly activated silica gel ("Davison" grade 923, 100–200 mesh, 60 g), packed in light petroleum. TLC examination of the fractions eluted with benzene–ether (4:1–1:1) indicated that most of them were mixtures of O-triacetyl-*cis*-brazilane (3) and the bi-brazilanyl derivative (7); only one fraction crystallized spontaneously and was, after crystallization from EtOH, identified as anhydro-O-triacetylbrazilin (6, 65 mg), m.p. and mixed m. p. with an authentic specimen 204–6° (sintering and discolouring from 185°). Since this compound had virtually the same R_f value as the dimer it was not immediately detected in the other fractions. These were induced to crystallize by triturating with ether and methylene dichloride, and allowing the solvent to evaporate at room temp; after oily material had been removed, fractional crystallization of the residues from benzene–light petroleum or methylene chloride–light petroleum (b.p. 40–60°) gave the bi-brazilanyl derivative (7, 64 mg), m.p. 230° (dec.) and O-triacetyl-*cis*-brazilane (3, 262 mg), m.p. and mixed m.p. with an authentic specimen 173–5°. The structure of all three compounds was confirmed by NMR (for details see under the appropriate compounds). The composition of the remaining material (1·27 g), comprising the residues from the mother liquors and the oily products, was estimated by NMR, and the calculated and weighed amounts combined. The distribution of the reaction products at 88% conversion of brazilein thereby arrived at was: 55% O-triacetyl-*cis*-brazilane (3), 40% bi-O-triacetyl-*cis*-brazilan-4-yl (7) and 5% anhydro-O-triacetylbrazilin (6).

O-*Triacetylbrazilone* (5) *from bi-O-triacetyl*-cis-*brazilan-4-yl* (7)

A soln of CrO_3 (0·5 g) in water (0·5 ml) and glacial AcOH (5 ml) was added dropwise over a period of 20 min to a magnetically stirred suspension of 7(556 mg)in AcOH (20 ml) at 50°, and the soln stirred at this temp for a further 30 min. After dilution with water (20 ml) and standing for 1 h at 0° unchanged starting material (220 mg) was removed by filtration, washed with water, and the filtrate and washings were evaporated to dryness under reduced pressure at 50°. The resulting pale gum, after leaching with warm light petroleum, crystallized immediately on addition of MeOH to give O-triacetylbrazilone (46 mg, 13%) as colourless needles, m.p. 187° (dec.), as reported.[5] undepressed on admixture with a specimen prepared from O-triacetylbrazilin; ν_{max} 1768 ($CH_3.\underline{CO}$–), 1722 (–$CH_2.\underline{CO}.CH_2$–), and 1645 cm^{-1} ($Ar.\underline{CO}.Ar$); NMR (60 MHz), τ 5·43 (2H, s, –$CO.C\underline{H}_2.O$–) and 6·32 (2H, s, $Ar.C\underline{H}_2.CO$–).

Anhydro-O-*triacetylbrazilin* (6)

(a) *From* O-*triacetylbrazilin* (4, R = OH). O-Triacetylbrazilin was most conveniently prepared by treating a soln of brazilin in NaOH aq, internally cooled with crushed ice, with a slight excess of Ac_2O. The yellow amorphous solid was washed with water, dissolved in benzene, and the soln filtered, dried, and evaporated. The triacetate crystallized (with 1 EtOH) from EtOH as pale yellow prisms (70%), m.p. 112° (dec.), reported[4] m.p. 108° (dec.); when the alcohol of crystallization was removed the compound became a hard, clear resin.

Tosyl chloride (2·79 g, 14·58 mmol) was added in small portions to a magnetically stirred soln of alcohol-free triacetylbrazilin (3 g, 7·29 mmol) in dry pyridine (20 ml) at 0°. After 5 days at 5° (refrigerator) and 3 days at room temp the mixture was poured into ice-cold HCl, the product collected in methylene chloride, and the washed and dried extract evaporated under reduced pressure at 20°. The *tosylate* (4, R = tosyl; 0·87 g, 21%) separated from EtOH as colourless prisms, m.p. 144–6° (Found: C, 61·0; H, 4·6; S, 5·7. $C_{29}H_{26}O_{10}S$ requires: C, 61·4; H, 4·6; S, 5·7%).

The tosylate (0·5 g) was boiled with pyridine (5 ml) under N_2 for 1 h, the soln poured into 6N HCl, and the ppt. crystallized form CH_2Cl_2–EtOH to give anhydro-O-triacetylbrazilin (192 mg, 55%) as pale cream leaflets, m.p. 206° (sintering and discolouring from 188°); NMR (60 MHz), τ 4·90 (2H, s, –$CH_2.O$–) and 6·68 (2H, s, $Ar.\underline{CH_2}$–) (Found: C, 66·9; H, 4·6. Calc. for $C_{22}H_{18}O_7$: C, 67·0; H, 4·6%).

(b) *From brazilein.* The following modification gave a much cleaner product than the original procedure.[8] A mixture of brazilein (4 g), Zn dust (30 g), fused NaOAc (4 g), and Ac_2O (80 ml) was refluxed with stirring under N_2 for 1·5 h. Zn dust was filtered from the hot mixture and washed with AcOH, and the filtrate poured into water (800 ml). After standing overnight the ppt was collected, and thoroughly washed with water and EtOH; crystallization from EtOAc–EtOH gave anhydro-O-triacetylbrazilin (3·35 g, 60%) as pale yellow hexagonal prisms, m.p. 206–8° (sintering and discolouring from 190°), reported[8] m.p. 190–4° (discolouring from 170°); the compound was identical with the specimen described above (mixed m.p., IR and NMR spectra).

O-*Triacetyl*-cis-*brazilane* (3)

Hydrogenation of a soln of the foregoing compound (2 g) in EtOAc (150 ml) in the presence of 2% palladium chloride on strontium carbonate (0·3 g) gave O-triacetyl-*cis*-brazilane (1·82 g, 90%), m.p. 173–5° (colourless prisms from MeOH). reported[2,3] m.p. 166–7°; λ_{max} 278·5 nm (ϵ 4600); NMR (220 MHz), τ 2·63 (1H, d, H-5), 2·86 (1H, s, H-4′ or H-7′), 2·95 (1H, s, H-4′ or H-7′), 3·28 (1H, dd, H-6), 3·39 (1H, d, H-8), 5·71 (1H, d, J_{34} 7·0 Hz, H-4), 5·88 (1H, dd, $J_{2\alpha 2\beta}$ −11·25, $J_{2\beta 3}$ 5·0 Hz, H-2β), 6·38 (1H, t, $J_{2\alpha 2\beta}$ −11·25, $J_{2\alpha 3}$ 10·0 Hz, H-2α), 6·80 (1H, dd, $J_{1'\alpha 1'\beta}$ −16·5, $J_{31'\beta}$ 7·0 Hz, H-1′β), 7·06 (1H, m, J_{34} 7·0, $J_{2\alpha 3}$ 10·0, $J_{2\beta 3}$ 5·0, $J_{31'\alpha}$ 2·0. $J_{31'\beta}$ 7·0 Hz, H-3), 7·34 (1H, dd, $J_{1'\alpha 1'\beta}$ −16·5, $J_{31'\beta}$ 2·0 Hz, H-1′α), 7·74 (9H, s, $3C\underline{H}_3.CO$).

Bi-O-trimethyl-cis-*brazilan-4-yl* (8)

The following conditions were found preferable to those previously described.[2] Methanolic NaOH aq and Me_2SO_4 were added gradually and alternately to a magnetically stirred soln of 7(211 mg) in THF under N_2 at 70° (bath temp) until no further colour change occurred. The yellow soln was diluted with water (150 ml), and after 15 min the product collected in benzene. After thorough washing the extract was evaporated to dryness, the partly crystalline reddish-brown residue dissolved in benzene and absorbed on neutral alumina ("Woelm" activity grade 1, 10 g). The product was eluted with benzene, and after twice crystallizing from MeOH the *compound* **8** was obtained as colourless prisms (110 mg). m.p. 192–4°, reported[2] m.p. 188–90° (Found: C, 73·3; H, 6·1. $C_{38}H_{38}O_6$ requires: C, 73·4; H, 6·1%).

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