Modification of the Structure of Bussein

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Summary The structure of bussein has been modified to (IIa)/(IIb) on the basis of the single-frequency decoupled ^{13}C n.m.r. spectra of a derivative.

BUSSEIN, m.p. 300—304°, was first isolated from the timber of *Entandrophragma bussei* Harms. and *E. caudatum* Sprague.[1] It is a mixture of bussein A, $C_{44}H_{56}O_{18}$ and B, $C_{43}H_{54}O_{18}$, to which structures (Ia) and (Ib) were assigned, respectively,[2] Our ^{1}H and ^{13}C n.m.r. studies now indicate that bussein A and B should be represented by structures (IIa) and (IIb).

The ^{13}C n.m.r. peaks of orthoesters and hemiorthoesters†

† The resonance of orthoesters should be similar to that of hemiorthoesters judged from the similarities between the chemical shifts of acetals and hemiacetals. For example, it is at 92·9 p.p.m. in sucrose and at 92·8 p.p.m. in glucose: L. F. Johnson and W. C. Jankowski, 'Carbon-13 NMR Spectra,' Wiley-Interscience, New York, 1972, pp. 443, 197.

are quite characteristic and appear around 119 p.p.m., *e.g.*, procerin 118·6 p.p.m.,[3] utilin[4] 119·2 p.p.m. However, the ^{13}C n.m.r. spectrum of bussein‡ (Table) shows only one peak at 118·9 p.p.m.; except for the furan resonances there are no other peaks in this region.

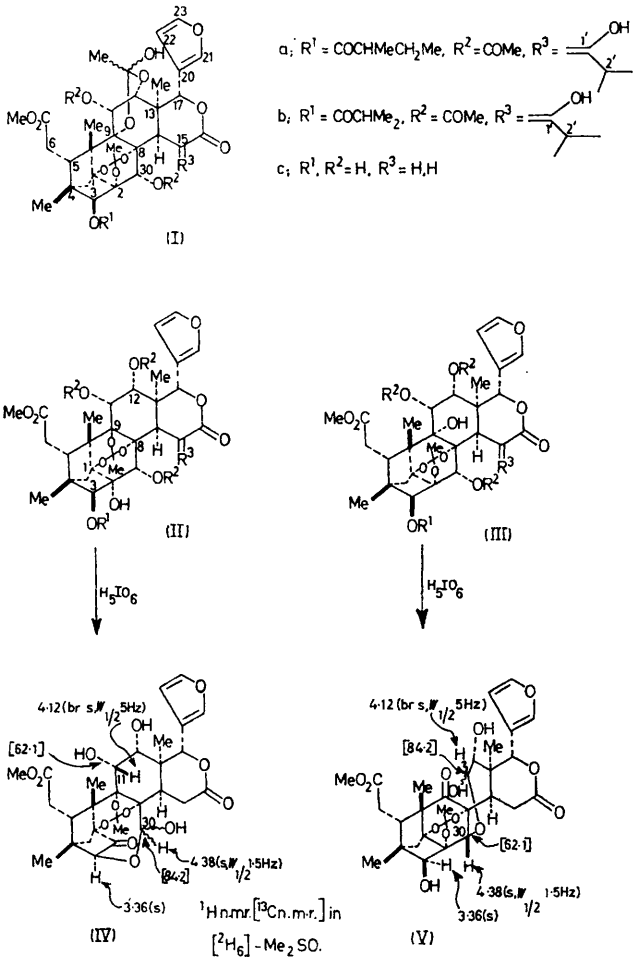
Modification of the bussein structure by opening of the hemiorthoester group accounts for this discrepancy and for the presence of an extra acetoxy carbonyl peak in the spectrum. The ^1H n.m.r. peak due to the extra acetoxy methyl group was not recognized previously since it appears at the anomalous position of 1·63 p.p.m. ($CDCl_3$).[5] Molecular models show that the 12-acetoxy methyl lies below the plane of the furan ring; hydrogenation of the furan ring shifts this peak to the more characteritsic position of 2·08 p.p.m.[2b].

TABLE. ^{13}C n.m.r. of bussein A/B

Carbon types	Number of carbons	Chemical shifts
Ester carbonyls and C(1′)	7	183·2, 176·1, 172·5, 170·3, 169·1, 168·6, 168·4
Furan	4	142·6, 141·2, [C(21) and C(23)], 121·9 [C(20)], 109·8 [C(22)]
Orthoester	1	118·9
C(15)	1	90·8
C–O (quaternary)	4	84·9, 83·3, 79·6, 77·2
CH–O	5	82·9 [C(3)], 73·9, 70·0, 70·0, 69·0
CO_2Me	1	51·8
Saturated (quaternary)	3	45·7, 45·7, 44·9
Methine	4	43·6, 41·4, 36·9, 30·2
Methylene	3	39·8, 33·2, 26·5[a]
Methyl	11	20·9, 20·7, 20·7, 20·3, 19·8, 18·5, 17·9, 16·7, 15·9, 14·2, 11·6
Total:	44	

[a] This peak is due to the extra methylene contained in the 3-acyl group of bussein A. All other peaks overlapped for bussein A and B.

The modification leads to two possible structures for bussein, (IIa/IIb) or (IIIa/IIIb) which only differ in the point of attachment of the orthoester group and a hydroxy group. Reaction of the hydrolysis product of bussein, (IIc) or (IIIc), with periodate yielded a product, m.p. 227—229°, which can be depicted either as (IV) or (V). Both structures are plausible from the ^1H n.m.r. and the proton-noise-decoupled ^{13}C n.m.r. (JEOL PS-100, 30 mg sample) spectra. However, ^{13}C n.m.r. analysis using single frequency decoupling showed that (V) is incorrect. Single frequency irradiation of the sharp ^1H n.m.r. singlet at 4·38 p.p.m. ($W_{1/2}$ 1·5 Hz, 30-H) decoupled the 84·2 p.p.m. ^{13}C n.m.r. doublet, while irradiation of the broad singlet at 4·12 p.p.m. ($W_{1/2}$ 5 Hz, 11-H) decoupled the 62·1 p.p.m. doublet. These results are consistent with structure (IV), but not with (V), and therefore bussein should be represented by (IIa/IIb). Furthermore, acetylation of the cleavage product only yielded the 11,12-diacetate. This is unlike the hydrolysis product (IIc) (or IIIc), which is readily acetylated at 3-OH.



Thus bussein is a complex limonoid with an orthoester group at C(1)/C(8)/C(9) as in phragmalin[6] (also from *E. caudatum* Sprague) and pseudrelone C.[7]

We thank the Swiss National Science Foundation and the National Institutes of Health for support.

(*Received*, 3*rd April* 1975; *Com.* 380.)

‡ ^{13}C n.m.r. assignments of bussein in ref. 3 necessarily require some revisions.

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