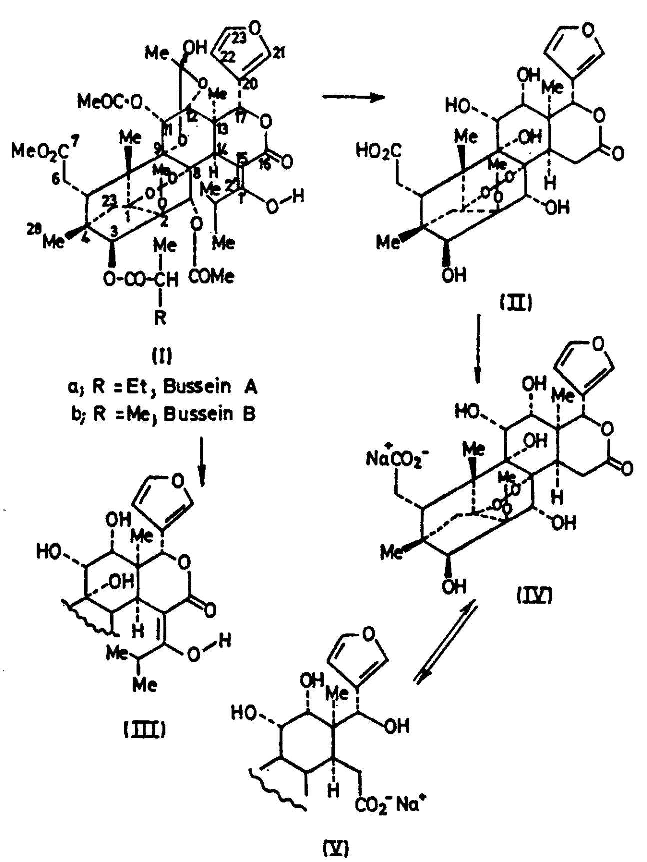
Structure of the Tetranortriterpene Bussein

By R. Hänni and Ch. Tamm*
(*Institut für Organische Chemie der Universität Basel, Basel, Switzerland*)

Summary Bussein is shown to be a mixture of bussein A, $C_{44}H_{56}O_{18}$, and bussein B, $C_{43}H_{54}O_{18}$; structure (Ia) is proposed for bussein A and structure (Ib) for bussein B.

Bussein is a crystalline compound isolated from the timber of *Entandrophragma bussei* Harms. and *Entandrophragma caudatum* Sprague,[1] and has been concluded to contain, among others, three acetyl, one isobutyryl, and one 2-methylbutyryl groups.[2,3] We have found that bussein is a mixture of two components, *i.e.* bussein A, $C_{44}H_{56}O_{18}$, and bussein B, $C_{43}H_{54}O_{18}$, to which structures (Ia) and (Ib), respectively, are assigned. The mass spectrum of a crystalline sample, m.p. 300—304°; $[\alpha]^{22}_{D}$ −59° ± 2° ($CHCl_3$), revealed two molecular ions, *m/e* 872 and 858. A peak due to loss of isobutyrate ($M^+ - 71$) is observed from both molecular ions, but one due to loss of 2-methylbutyrate is observed only from (Ia), showing that bussein A (Ia) contains a 2-methylbutyryloxy-group at C-3, bussein B (Ib) an isobutyryloxy-group. The u.v. spectrum (EtOH) of bussein shows λ_{max} 207 (log ϵ 3·86) (furan) and 268 nm (log ϵ 4·02) (shifts to 288·5 nm, log ϵ 4·21, on addition of NaOH) (enolizable β-dicarbonyl). The i.r. spectrum indicates the presence of several carbonyl and acetate groups, and the n.m.r. spectrum (100 MHz; $CHCl_3$) is interpreted as follows (δ values in p.p.m.; *J* in Hz): 2·94 (m, *J* 6·5, 2′-H), 1·37 (d, *J* 6·5, 3′-H), 4·98 (s, 3-H), 1·92 br (s, 5-H), 2·76 (m, 6-H), 5·61 (d, *J* 2·5, 11-H), 4·62 (d, *J* 2·5, 12-H), 3·30 (s, 14-H), 5·81 (s, 17-H), 3·15 and 2·55 (d, *J* 10, 29-H), 5·48 (s, 30-H), 7·64, 7·30, and 6·45 (furan), 1·63 (hemi- and ortho-acetate), 1·54, 1·28, and 1·00 (Me), 2·17 and 2·00, 3·74 (CO_2Me), and 13·93 (enol). The majority of the known tetranortriterpenes contain 4 methyl groups. In bussein the fourth methyl group is replaced by a methylene group (C-29) forming an additional bridge from C-1 to C-4 as in utilin[5] and entandrophragmin.[6] Exceptions are, *e.g.*, hirtin, nimbin, and utilin.[3—5]



(I)

a; R = Et, Bussein A

b; R = Me, Bussein B

(II)

(III)

(IV)

(V)

Total hydrolysis of bussein with NaOH in MeOH yielded 5 equiv. of volatile acids [3 equiv. of acetic acid, 1·5 equiv. of isobutyric acid, and 0·5 equiv. of (*R*)-(−)-2-methylbutyric acid], identified by the n.m.r. spectra (D_2O) of the sodium salts, in addition to the hydroxy-acid (II), $C_{28}H_{34}O_{13}$, which possesses one carboxy-group. Further treatment of either bussein or the hydrolysis product (II) with a known excess of NaOH and retitration with HCl revealed an additional lactone group. This reaction yielded the sodium salts (IV) and (V), respectively. The hydroxy-acid (II) contains an orthoacetate group resistent to hydrolysis, δ (Me) 1·65 p.p.m. [(CD_3SO)]. Its position was deduced from the properties of the products obtained by the HIO_4 cleavage of the methyl ester of acid (II). Partial hydrolysis of bussein with conc. aqueous NH_3 in MeOH led to compound (III), which contains one acetyl group less than the starting material. Further hydrolysis of (III) with NaOH in MeOH gave 3 equiv. of volatile acids, only 1 equiv. being acetic acid. CrO_3-oxidation of (III) and additional products of partial hydrolyses established hydroxy-groups at C-3, C-11, and C-12, which are acylated in the busseins. In compound (III) the hemiorthoacetate group at C-9 and C-12 and the 11-acetoxy-group have disappeared, the molecular ion being at *m/e* 788 corresponding to the loss of 2 mass units of 42 each. The hemiorthoacetate group was regenerated by treatment of (III) with acetic anhydride. Its position as well as the 11α-acetoxy-group was established by spin-decoupling experiments with bussein.

The presence of the enolized β-keto-lactone system was demonstrated by appearance of a singlet at δ 13·13 p.p.m. due to an enol proton exchangeable by D_2O in the n.m.r. spectrum of bussein, by the presence of bands at 1570 and 1400 cm^{-1} (CO_2^-) and by the absence of a C=O stretching in the i.r. spectrum (KBr) of the sodium salt (V). The latter observation excludes an enolized α-acylcyclohexanone system as anticipated earlier.[3] The balance of the oxygen atoms is not compatible with a β-keto-ester group. The n.m.r. spectrum of the product obtained by $LiAlH_4$-reduction and subsequent acetylation of bussein possessing a new hemiacetal group confirmed this conclusion. The mass spectra of bussein and the hydrolysis product (III) are also in agreement with the presence of a β-ketol-actone group. They do not exhibit the $M^+ - 96$ peak due to the loss of β-furfuraldehyde by an α-cleavage of the unsubstituted lactone ring,[7] a fragmentation characteristic of most limonoids.

Chemical evidence for furan ring C-17 was adduced by degradation of bussein with ozone.

The busseins A (Ia) and B (Ib) are further members of the meliacin family, characterized by a highly complex structure related to utilin[5] and phragmalin.[8]

We thank Professor D. A. H. Taylor, Ibadan, Nigeria, for a gift of bussein and for discussions. The work was supported by the Swiss National Science Foundation.

(*Received, 14th September* 1972; *Com.* 1587.)

---

[1] D. A. H. Taylor, *J. Chem. Soc.* (*C*), 1965, 3495; G. A. Adesida and D. A. H. Taylor, *Phytochemistry*, 1967, **6**, 1429.

[2] D. H. Calam and D. A. H. Taylor, *J. Chem. Soc.* (*C*), 1966, 949.

[3] D. A. H. Taylor, *Chem. and Ind.*, 1967, 582.

[4] W. R. Chan and D. R. Taylor, *Chem. Comm.*, 1966, 206; R. Henderson, R. McCrindle, K. H. Overton, M. Harris, and D. W. Turner, *Proc. Chem. Soc.*, 1963, 269; C. R. Narayanan, R. V. Pachapurkar, S. K. Pradhan, V. R. Shah, and S. Narasimhan, *Chem. and Ind.*, 1964, 322.

[5] H. R. Harrison, O. J. R. Hodder, C. W. L. Bevan, D. A. H. Taylor, and T. G. Halsall, *Chem. Comm.*, 1970, 1388.

[6] E. O. Arene, C. W. L. Bevan, J. W. Powell, D. A. H. Taylor, and K. Wragg, *Chem. Comm.*, 1966, 627.

[7] *Cf.* H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1964, p. 10.

[8] R. R. Arndt and W. H. Baarschers, *Tetrahedron*, 1972, **28**, 2333.