The imidazole residues exist in the N^{τ}–H tautomeric form* in which the non-protonated nitrogen (N^{π}) is adjacent to the side chain. This differs from histamine base (as recrystallized from benzene) (Bonnet & Ibers, 1973) but is the same form as found in the crystal of L-histidine (Madden, McGandy, Seeman, Harding & Hoy, 1972; Madden, McGandy & Seeman, 1972), *O*-methyl-L-pyroglutamyl-L-histidine (Cotrait & Allard, 1973), 6-histaminopurine dihydrate (Thewalt & Bugg, 1972) and the H_2-receptor antagonists, burimamide (Kamenar, Prout & Ganellin, 1973) and *N*-methyl-*N'*-{2-(5-methylimidazol-4-yl)methylthioethyl}-thiourea (Critchley, S. R., Prout, K. & Ganellin, C. R. unpublished work).

The N^{τ}–H tautomer is generally regarded as being the biologically active (H_1-receptor) species of histamine and is the preferred form in aqueous solution, although, at 37 °C the free-energy difference between the two tautomers is less than 1 kcal mol^{-1} (Ganellin, 1973*b*).

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* Following the IUPAC–IUB Commission on Biochemical Nomenclature 1972 recommendations for histidine, the imidazole N nearer the side chain is designated N^{π}, and the one farther is N^{τ} (Black & Ganellin, 1974).

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Jujubogenin *p*-Bromobenzoate

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Abstract. $C_{37}H_{51}O_5Br.\frac{1}{2}AcOEt$, m.p. 256–258 °C, triclinic, space group $P1$, with $a=16{\cdot}74$ (1), $b=15{\cdot}29$ (1), $c=7{\cdot}486$ (5) Å, $\alpha=94{\cdot}25$ (1), $\beta=102{\cdot}00$ (1), $\gamma=100{\cdot}98$ (1)°, $Z=2$, $D_x=1{\cdot}268$ g cm^{-3}, μ(Cu $K\alpha$)= 22 cm^{-1}. The structure was solved by the heavy-atom anomalous dispersion method and refined to an R value of 0·076 for 1725 observed reflexions. The chemical structure of jujubogenin has been established as 3β,20*S*-dihydroxy-16β(23*R*),16α(30)-dioxidodammar-24-ene. The dimensions and conformations of the two crystallographically independent molecules involved in the asymmetric unit generally agree with each other.

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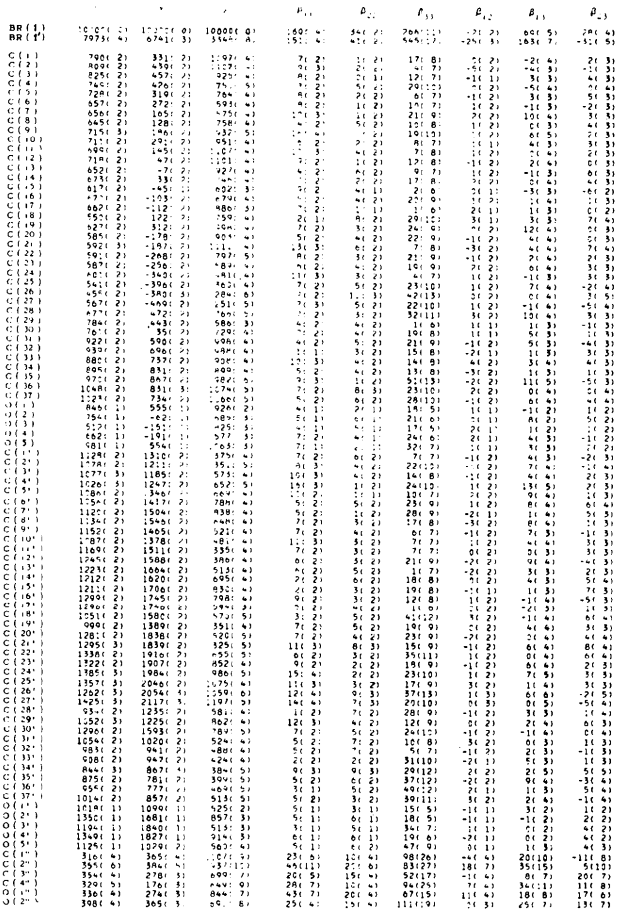
Introduction. Jujubogenin, $C_{30}H_{48}O_4$, is the main sapogenin obtained by periodate oxidation of jujuboside B isolated from *Zizyphus jujuba* Mill. and hovenoside G from *Hovenia dulcis* Thunb. (Kawai, Akiyama, Ogihara & Shibata, 1974). The *p*-bromobenzoate was recrystallized from ethyl acetate solution as colourless

plates elongated along the *c* axis. The intensity data were collected by a Philips four-circle diffractometer using graphite monochromated Cu $K\alpha$ radiation The size of the crystal was about $0{\cdot}1 \times 0{\cdot}2 \times 0{\cdot}2$ mm. Of the 2223 independent (excluding Friedel) reflexions within $2\theta = 80°$, 1725 planes along with their 1007 Friedel reflexions were measured as being above the 2σ level and these were used for the present structure determination. Intensities were corrected for Lorentz and polarization factors and were put on an absolute scale by Wilson's method. No absorption correction was applied.

The positions of the two bromine atoms were determined from a Patterson function. Ambiguity in phase determination for the present structure (two heavy atoms are related by a false centre of symmetry in an acentric space group) was removed by applying the anomalous dispersion method (Hall & Maslen, 1965). The first Fourier map showed about 60 atoms in an asymmetric unit and only one additional set of Fourier and difference Fourier syntheses was necessary to establish the whole structure with correct absolute configuration. Refinement was by the block-diagonal least-squares method using the *HBLS* program of Okaya & Ashida (1967). Eleven cycles of calculation gave an R value of 0·076 for 1725 observed reflexions. The weighting scheme was: $w=1$ when $F_o \geq 5$, $w=0$ otherwise. Atomic scattering factors were those cited as SX-6,7,8 and 71 in *International Tables for X-ray Crystallography* (1962). No attempt was made either to include hydrogen atoms or to correct for anomalous dispersion effects during the refinement. The final atomic parameters are listed in Table 1.*

Table 1. *Atomic parameters* ($\times 10^4$ *for bromine and* $\times 10^3$ *for other atoms*)

Temperature factors are of the form $T=\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$. Unprimed atoms are those of molecule I, primed atoms are of I′ and double primed atoms are of ethyl acetate. To represent the correct absolute configuration the coordinates should be referred to the right-hand coordinate system.



Discussion. The structure of jujubogenin was established as 3β,20*S*-dihydroxy-16β(23*R*), 16α(30)-dioxidodammar-24-ene, as shown in Fig. 1. The configuration at C(20) is the same as that in 20*S*-protopanaxadiol, a genuine sapogenin of *Panax ginseng* C. A. Mayer (Tanaka, Nagai, Ohsawa, Tanaka & Shibata, 1967) and is opposite to that in bacogenin-A (Kawai, Iitaka, Shibata, Kulshreshtha & Rastogi, 1973). The bond lengths and angles averaged over the two crystallographically independent molecules, I and I′, are shown in Fig. 1. The differences in the corresponding lengths and angles between I and I′ are shown in Table 2 along with their e.s.d.'s. Each *A*, *B* and C six-membered ring adopts a chair form, the five-membered ring *D* is an envelope, and the tetrahydropyrane rings *E* and *G* are a boat and a chair respectively. The endocyclic torsion angles along the bonds involved in each *A*, *B*, C, *D*, *F* and *G* ring are shown in Fig. 1. The differences (Δ) in the corresponding torsion angles between molecules I and I′ range from 0 to 18·9° with the average value 4·4°; exceptions are Δ[O(1)–C(3)–C(4)–C(28)] = 28° and Δ[O(1)–C(3)–C(4)–C(29)] = 22°. The junctions of the rings, *A*/*B*, *B*/*C* and *C*/*D* are all *trans*.

Table 2. *Average differences* (Δ) *in the corresponding bond lengths and angles between* (I) *and* (I′)

	Bond length		Bond angle	
Jujubogenin	Δ	σ(mean)	Δ	σ(mean)
endocyclic	0·057 Å	0·043 Å	2·81°	2·47°
exocyclic	0·049	0·047	4·16	2·70
Benzoate	0·115	0·043	5·78	2·93

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30596 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

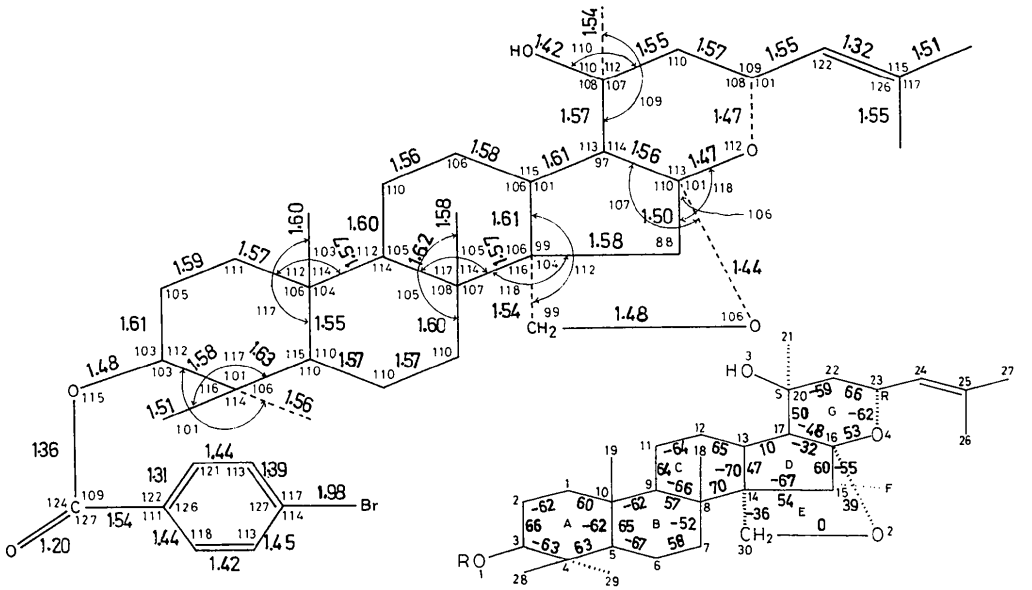


Fig. 1. Bond lengths (Å), angles (°) and endocyclic torsion angles (°) averaged for the corresponding bonds in molecules I and **I'**.

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1-Methyl-3,3,5,5-tetraphenyl-1-thia-3,5-diphospha^{V}-2,6-diazin

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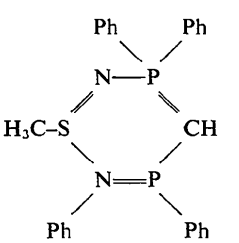
Abstract. $C_{26}H_{24}N_2P_2S$, orthorhombic, *Pbnm*, $a=9{\cdot}473$ (4), $b=11{\cdot}551$ (5), $c=21{\cdot}453$ (9) Å, $Z=4$, $D_c=1{\cdot}30$ g cm^{-3}. The structure was refined by least-squares methods to $R=6{\cdot}3$ %. The molecule has a mirror plane. The six-membered CN_2P_2S-ring is puckered. All bond lengths in the ring are between those of single and double bonds.

Einleitung. Appel & Hänssgen (1967) synthetisierten ein neues sechsgliedriges Ringsystem, das Kohlenstoff, Schwefel, Stickstoff und Phosphor als Ringglieder enthält. Von einem Vertreter dieser Gruppe, vom 1-Methyl-3,3,5,5-tetraphenyl-1-thia-3,6-diphospha^{V}-2,6-diazin (I) wurde die Struktur röntgenographisch bestimmt.



(I)