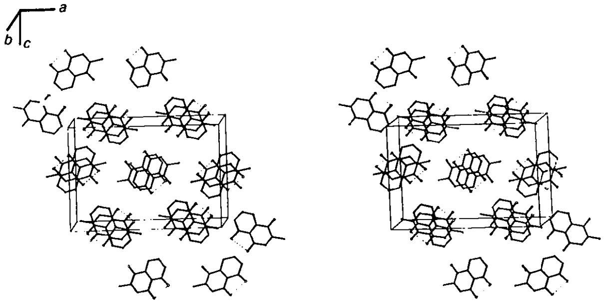

Fig. 3. Stereo packing diagram of the molecules.

between theoretical values for centrosymmetric and noncentrosymmetric distributions.

The planes of molecule *B* are stacked almost perpendicular to the *b* axis with a constant interplanar distance of 3·53 (2) Å. The naphthoquinone ring planes of *A* and *B* are at an angle of 17·2° to each other. The molecular layers of *A* are arranged at alternate distances of 3·52 (2) and 3·38 (2) Å.

A stereo plot of the molecule down the *b* axis with 10° rotation around both *x* and *z* axes using the molecular plotting program of Radhakrishnan (1982) is given in Fig. 3. In each of the molecules the hydrogen of the hydroxy group forms an intramolecular hydrogen bond with the carbonyl group. In molecule *A* the O(3)···O(2) distance is 2·599 (7) Å, H(O3)···O(2) is 1·87 (8) Å and the O(3)—H(O3)···O(2) angle is 130 (5)°. In molecular *B* O(3′)···O(2′) is 2·570 (7) Å, H(O3′)···O(2′) is 1·71 (15) Å and the O(3′)—H(O3′)···O(2′) angle is 161 (11)°. The crystal packing is stabilized by van der Waals forces.

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Structure of Ginkgolide A (BN52020) Monohydrate and Ginkgolide C (BN52022).Ethanol.1·5Hydrate, Isolated from *Ginkgo biloba* L.

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Abstract. Ginkgolide A monohydrate: 3-(1,1-dimethylethyl)hexahydro-4,7b-dihydroxy-8-methyl-9*H*-1,7a-(epoxymethano)-1*H*,6a*H*-cyclopenta[*c*]furo[2,3-*b*]furo[3′,2′:3,4]cyclopenta[1,2-*d*]furan-5,9,12(4*H*)-trione monohydrate, $C_{20}H_{24}O_9.H_2O$, $M_r = 426{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}9906\,(3)$, $b = 12{\cdot}4256\,(10)$, $c = 17{\cdot}8140\,(11)$ Å, $V = 1990{\cdot}1\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}423$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 8{\cdot}2$ cm^{-1}, $T = 290$ K, $F(000) = 904$, final $R = 0{\cdot}042$ for 1399 observed reflections. Ginkgolide C.ethanol.1·5hydrate: 3-(1,1-dimethylethyl)hexahydro-2,4,7b,11-tetrahydroxyl-8-methyl-9*H*-1,7a-(epoxymethano)-1*H*,6a*H*-cyclopenta[*c*]furo[2,3-*b*]furo[3′,2′:3,4]cyclopenta[1,2-*d*]furan-5,9,12(4*H*)-trione.ethanol.1·5hydrate, $C_{20}H_{24}O_{11}.C_2H_6O.1{\cdot}5H_2O$, $M_r = 513{\cdot}5$, monoclinic, $P2_1$, $a = 12{\cdot}9668\,(5)$, $b = 13{\cdot}1218\,(6)$, $c = 15{\cdot}3083\,(5)$ Å, $\beta = 112{\cdot}95\,(3)°$, $V = 2398{\cdot}5\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}422$ g cm^{-3}, $\mu(\mathrm{Cu}\ K\alpha) = 9{\cdot}1$ cm^{-1}, $F(000) = 1092$,

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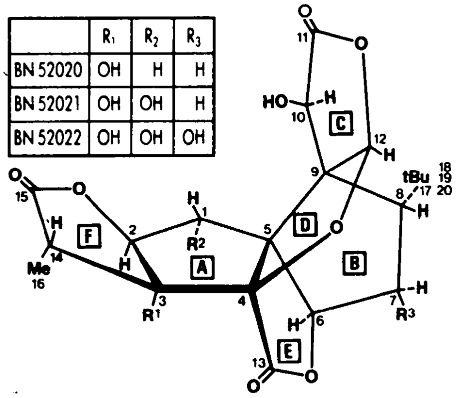
final R = 0·074 for 2964 observed reflections. In both structures, conformations of the rings are very similar to those in ginkgolide B, except for rings A and F of ginkgolide A where there is no hydroxyl substitution in the 2-position: the intramolecular OH···O hydrogen bond occurring in ginkgolides B and C is no longer possible in A. The cohesion of the crystals results from van der Waals interactions and O—H···O hydrogen bonds involving water and (in ginkgolide C) ethanol molecules. In ginkgolide A, there is a short intermolecular O···O contact of 2·859 (6) Å between a lactone ring and a ketone.

Introduction. Ginkgolides A, B and C (BN52020, BN52021 and BN52022, respectively) (Fig. 1) are terpenes isolated from the Chinese tree *Ginkgo biloba* L. They constitute a family of potent specific antagonists of the platelet-activating factor (PAF, PAF/acether, AGEPC). BN52021 is the most active and BN52022 the least potent compound, suggesting that the presence of a hydroxyl group close to the lipophilic moiety counteracts the antagonist property (Braquet & Godfroid, 1986). The structure of ginkgolide B (BN52021) has been determined by Dupont, Dideberg, Germain & Braquet (1986). A communication on the structure of the mono-*p*-bromobenzoate of ginkgolide A was published by Sakabe, Takada & Okabe (1967) but the atomic coordinates were not given. The final R value was 0·19 and a redetermination of the crystal structure of BN52020 is therefore necessary. The molecular structures of ginkgolides constitute rigid models which can be used as reference for the comparison of the conformations of PAF and its antagonists.

Experimental. Ginkgolides A and C were prepared from a standardized extract (GBE761) prepared from dried and stabilized leaves of *Ginkgo biloba* L. (IHP–IPSEN Research Laboratories, Paris, France). The extraction was performed according to the procedure previously described by Okabe, Yamada, Yamarura & Takada (1967). Further details concerning the isolation, purification and characterization of BN52020 and BN52022 have been published elsewhere (Braquet, 1984). Crystallization by slow evaporation of an ethanol–acetone–water solution. Data collection: Siemens diffractometer, Cu $K\alpha$ radiation with monochromator ($2\theta = 26{\cdot}5°$), ω-scan mode. Two standard reflections showed no significant changes. Absorption corrections by empirical method of North, Phillips & Mathews (1968). BN52020: colourless crystal, 0·49 × 0·38 × 0·20 mm. Cell parameters determined by least-squares refinement from 36 reflections ($30{\cdot}1 \leq \theta \leq 35{\cdot}0°$). 1585 intensities collected ($4{\cdot}9 \leq 2\theta \leq 109{\cdot}8°$), 1399 unique reflections, all considered observed, $0 \leq h \leq 9$, $0 \leq k \leq 13$, $0 \leq l \leq 18$; $R_{\rm int} = 0{\cdot}01$. Minimum and maximum transmission coefficients 0·694 and 0·823; structure solved by direct methods with *SHELXS*86 (Sheldrick, 1986). Full-matrix refinement on F with *SHELX*76 (Sheldrick, 1976), 285 parameters. Anisotropic temperature factors for all non-H atoms, H atoms at calculated positions, except H involved in hydrogen bonds, obtained from difference synthesis. The absolute configuration was established by comparison with BN52021 (as also for BN52022). Final conventional $R(F) = 0{\cdot}042$, $wR = 0{\cdot}064$, $w = 1/[\sigma^2(F) + 0{\cdot}041374F^2]$. In final cycle of least-squares refinement max. $\Delta/\sigma \leq 0{\cdot}25$. Maximum and minimum heights in final ΔF synthesis 0·16 and −0·20 e Å^{-3}; atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974). BN52022: colourless crystal, 0·38 × 0·45 × 0·17 mm. Cell parameters determined by least-squares refinement from 22 reflections ($30{\cdot}0 \leq \theta \leq 34{\cdot}9°$). 3602 intensities collected ($6 \leq 2\theta \leq 110°$), 3111 unique reflections; $-13 \leq h \leq 12$, $0 \leq k \leq 13$, $0 \leq l \leq 14$; $R_{\rm int} = 0{\cdot}01$; 2964 considered as observed [$I > 2{\cdot}5\sigma(I)$]. Minimum and maximum transmission coefficients 0·666 and 0·819; structure solved by Patterson method with *SHELXS*86 (Sheldrick, 1986) and *PATSEE* (Egert & Sheldrick, 1985). Starting model used: BN52021 structure. The two independent molecules required a large number of refinement parameters (maximum 668). The blocked full-matrix approximation (*SHELX*76; Sheldrick, 1976) was used and only 22 O atoms were refined anisotropically to limit the ratio of number of parameters/number of reflections to a reasonable value. Accordingly, the final R values are relatively high. The other C and O atoms were refined isotropically. H atoms at calculated positions. Four of the eight H (OH) positions in BN52022 were estimated from a difference map and hydrogen-bond considerations. H(O1), H(O11), H(O21), H(O31), the H of water molecules and the hydroxy H of ethanol could not be placed unambiguously, the system of hydrogen bonds being rather complicated. Final conventional $R(F) = 0{\cdot}074$, $wR = 0{\cdot}087$, $w = 1/[\sigma^2(F) + 0{\cdot}05169F^2]$. In final cycle of



	R_1	R_2	R_3
BN 52020	OH	H	H
BN 52021	OH	OH	H
BN 52022	OH	OH	OH

Fig. 1. Formula of ginkgolides.

least-squares refinement, max. $\Delta/\sigma \leq 0{\cdot}4$; maximum and minimum heights in final ΔF synthesis +0·5 and −0·5 e Å^{-3}. The atomic parameters of both structures are listed in Table 1.* The atom numbering is defined in Figs. 1 and 2. C101, C102 and O102, C201, C202 and O202 are components of ethanol molecules. O100, O200 and O300 are water oxygens.

Table 1. *Fractional coordinates* (× 10^4) *with e.s.d.'s in parentheses and equivalent isotropic temperature factors* (Å^2) *of non-hydrogen atoms*

$B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$ where $\mathbf{a}_i$ is the direct unit-cell constant. The anisotropic thermal correction $\varphi(hkl) = \exp[-2\pi^2(U_{11}h^2a_1^{*2} + \cdots + 2\,U_{23}kla_2^*a_3^* + \cdots)]$.

In BN52022, atoms C1, ..., C20, and O1, ..., O11 refer to molecule *A*; C21, ..., C40, O21, ..., O31 are the corresponding atoms of molecule *B*.

	x	*y*	*z*	B_{eq}
BN52020				
C1	−2344 (5)	−3356 (3)	−6517 (2)	3·7 (1)
C2	−1371 (5)	−2646 (3)	−6031 (2)	3·4 (1)
C3	−530 (4)	−1874 (3)	−6546 (2)	3·3 (1)
C4	−1577 (4)	−1761 (3)	−7235 (2)	3·2 (1)
C5	−2568 (4)	−2752 (3)	−7276 (2)	3·2 (1)
C6	−1968 (5)	−3374 (4)	−7966 (2)	4·0 (1)
C7	−3279 (6)	−3485 (4)	−8498 (2)	4·0 (1)
C8	−4133 (5)	−2441 (3)	−8392 (2)	3·5 (1)
C9	−4111 (4)	−2291 (3)	−7516 (2)	3·0 (1)
C10	−5440 (5)	−2696 (3)	−7060 (2)	3·3 (1)
C11	−5329 (5)	−2037 (3)	−6345 (2)	3·4 (1)
C12	−4028 (4)	−1114 (3)	−7251 (2)	3·3 (1)
C13	−711 (5)	−1733 (4)	−7962 (2)	3·9 (1)
C14	−367 (5)	−853 (3)	−6072 (3)	4·0 (1)
C15	−1677 (5)	−952 (4)	−5540 (3)	3·9 (1)
C16	1074 (5)	−799 (4)	−5620 (3)	5·3 (1)
C17	−5635 (5)	−2345 (3)	−8849 (2)	3·9 (1)
C18	−6398 (5)	−1266 (4)	−8691 (3)	4·6 (1)
C19	−6713 (6)	−3289 (4)	−8707 (3)	4·9 (1)
C20	−5196 (6)	−2353 (5)	−9675 (3)	5·6 (1)
O2	814 (3)	−2298 (3)	−6827 (2)	4·0 (1)
O3	−5492 (3)	−3810 (2)	−6949 (2)	4·0 (1)
O4	−5770 (4)	−2258 (3)	−5733 (2)	4·8 (1)
O5	−4667 (3)	−1082 (2)	−6510 (2)	3·7 (1)
O6	−2515 (3)	−822 (2)	−7207 (2)	3·5 (1)
O7	−858 (4)	−2674 (3)	−8324 (2)	4·5 (1)
O8	−20 (3)	−988 (3)	−8224 (2)	4·8 (1)
O9	−2139 (4)	−278 (3)	−5111 (2)	5·0 (1)
O10	−2280 (3)	−1944 (2)	−5566 (2)	3·8 (1)
O100	−1783 (4)	−9208 (2)	−8726 (2)	4·3 (1)
BN52022				
C1	1411 (5)	1522 (1)	2640 (4)	3·4 (1)
C2	2630 (5)	1191 (6)	2978 (5)	3·7 (1)
C3	2814 (5)	863 (5)	2073 (4)	3·1 (1)
C4	1625 (5)	472 (5)	1377 (4)	3·2 (1)
C5	778 (5)	814 (5)	1812 (4)	3·0 (1)
C6	423 (5)	−189 (5)	2132 (4)	3·3 (1)
C7	−846 (5)	−269 (5)	1573 (5)	3·5 (1)
C8	−1050 (5)	225 (5)	623 (4)	3·3 (1)
C9	−277 (4)	1169 (5)	911 (4)	2·6 (1)
C10	−736 (5)	2205 (5)	1042 (4)	3·0 (1)
C11	43 (5)	2975 (5)	866 (4)	3·3 (1)
C12	280 (5)	1437 (5)	192 (4)	2·9 (1)
C13	1554 (5)	−658 (6)	1325 (5)	3·8 (1)
C14	3212 (5)	1875 (5)	1789 (4)	3·3 (1)
C15	3728 (5)	2414 (6)	2716 (5)	4·0 (1)
C16	3951 (6)	1752 (7)	1245 (5)	4·8 (1)
C17	−2296 (5)	355 (6)	−52 (5)	3·9 (1)
C18	−2430 (7)	995 (7)	−971 (6)	5·3 (1)
C19	−3020 (7)	827 (7)	411 (6)	5·2 (1)
C20	−2786 (7)	−697 (7)	−428 (6)	5·5 (1)
O1	1055 (4)	1520 (4)	3385 (3)	3·3 (1)
O2	3673 (4)	130 (4)	2265 (3)	3·6 (1)
O3	−832 (4)	2286 (4)	1918 (3)	3·2 (1)
O4	229 (4)	3829 (4)	1135 (4)	4·0 (2)
O5	555 (4)	2523 (4)	345 (3)	3·2 (1)
O6	1273 (3)	884 (4)	435 (3)	2·9 (1)
O7	960 (4)	−1024 (4)	1816 (3)	3·6 (1)
O8	1940 (4)	−1243 (4)	917 (4)	4·2 (2)
O9	4391 (4)	3135 (5)	2907 (4)	4·8 (2)
O10	3404 (4)	2026 (4)	3369 (3)	4·2 (1)
O11	−1244 (4)	−1281 (4)	1575 (4)	4·6 (2)
C101	4970 (12)	3867 (14)	8938 (10)	10·2 (2)
C102	5731 (10)	3552 (12)	9837 (9)	9·3 (2)
O102	6804 (5)	3959 (6)	10234 (5)	7·1 (1)
O100	5300 (4)	4218 (5)	4603 (4)	5·9 (1)
O200	7667 (5)	4421 (5)	5247 (4)	5·9 (1)
C21	367 (5)	1414 (5)	7496 (4)	3·2 (1)
C22	1251 (5)	737 (5)	8181 (4)	3·4 (1)
C23	1676 (5)	39 (5)	7591 (4)	3·1 (1)
C24	657 (5)	−10 (5)	6617 (4)	2·9 (1)
C25	−228 (4)	742 (5)	6643 (4)	2·6 (1)
C26	−1165 (5)	64 (5)	6711 (4)	3·2 (1)
C27	−2199 (5)	282 (5)	5863 (4)	3·3 (1)
C28	−1772 (5)	495 (5)	5050 (4)	3·0 (1)
C29	−705 (5)	1196 (5)	5610 (4)	3·0 (1)
C30	−869 (5)	2334 (6)	5553 (5)	3·8 (1)
C31	315 (6)	2750 (6)	5799 (5)	4·3 (1)
C32	279 (5)	1047 (5)	5308 (4)	3·2 (1)
C33	92 (5)	−1057 (5)	6453 (4)	3·4 (1)
C34	2690 (5)	615 (6)	7567 (5)	4·0 (1)
C35	3088 (7)	1186 (8)	8505 (6)	5·9 (1)
C36	3615 (7)	−77 (8)	7440 (7)	6·4 (1)
C37	−2639 (5)	807 (5)	4069 (5)	3·9 (1)
C38	−2050 (6)	1115 (7)	3421 (5)	4·9 (1)
C39	−3410 (7)	1665 (7)	4152 (6)	5·5 (1)
C40	−3349 (7)	−97 (7)	3631 (6)	5·4 (1)
O21	−314 (4)	1806 (4)	7962 (3)	3·9 (1)
O22	1933 (3)	−961 (4)	7969 (3)	3·1 (1)
O23	−1341 (4)	2719 (4)	6176 (3)	3·9 (1)
O24	687 (6)	3558 (5)	6026 (4)	5·6 (2)
O25	937 (4)	1965 (4)	5623 (3)	4·0 (1)
O26	942 (3)	223 (4)	5819 (3)	3·0 (1)
O27	−836 (3)	−1003 (3)	6645 (3)	2·8 (1)
O28	367 (4)	−1838 (4)	6196 (3)	3·5 (1)
O29	4001 (5)	1520 (6)	8975 (4)	7·1 (2)
O30	2230 (4)	1287 (4)	8814 (3)	4·4 (2)
O31	−3044 (4)	−404 (4)	5690 (4)	4·1 (1)
C201	5340 (17)	2033 (21)	6368 (14)	15·1 (4)
C202	6269 (12)	2627 (13)	6773 (10)	10·0 (2)
O202	6304 (6)	3646 (6)	6528 (5)	7·6 (1)
O300	2678 (5)	2739 (6)	4980 (5)	7·2 (1)

Discussion. Bond lengths are given in Table 2. All distances and angles are consistent with the expected values except in ethanol molecules of the BN52022 structure where methyl-group positions are probably disordered, resulting in the large temperature factors observed. Only some distances are significantly different $[(d_i^A - d_i^B)/(\sigma^2_{d_i^A} + \sigma^2_{d_i^B})^{1/2} > 3]$ in BN52022 (molecule *A*) and BN52022 *B*. Many of these deviations affect atoms of ring *B*, which is the most flexible one. A best molecular fit with program *BMFIT* (Nyburg, 1980) of the four molecules BN52021 *A* and *B*, BN52022 *A* and *B* (Fig. 3*a*) displays the slight divergences between them, which mainly result from the particular surroundings of each molecule. When the six rings are fitted, all distances between atoms of BN52021 *A* and the corresponding atoms of BN52021 *B* are less than 0·10 (2) Å. The largest distance between equivalent atoms of BN52021 *A* and BN52022 *A* is

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* Lists of structure factors, bond angles, anisotropic thermal parameters, H-atom positions, intermolecular distances, and Cremer–Pople parameters (of ginkgolide C) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44276 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0·17 (2) Å. The fit BN52021 *A* – BN52022 *B* gives a maximum deviation of 0·32 (2) Å, and all distances BN52022 *A* – BN52022 *B* are within the limit 0·33 (2) Å. The largest deviations involve the atoms O(2), O(4), O(9) and methyl carbons. The conformation of BN52020 is different from that of BN52021 and BN52022. The fit of the rings *B*, *C*, *D* and *E* of BN52021 *A* and BN52020 (Fig. 3*b*) shows that the deviations are located in rings *A* and *F*. The five internal dihedral angles of rings *A* are: C1—C2—C3—C4, 27·5 (4), C2—C3—C4—C5, −23·4 (4), C3—C4—C5—C1, 11·4 (4), C4—C5—C1—C2, 5·9 (4) and C5—C1—C2—C3, −21·3 (4)°. The torsional angle C1—C2—C3—O2 is −86·8 (4) and C1—C2—C3—C14 is 147·6 (4)°. The corresponding values in BN52021 *A* are respectively −29·3 (7), 11·0 (7), 10·1 (7) −28·7 (7), 36·5 (7), −150·8 (7) and 90·7 (7)°. In ring *F*, the signs of the internal torsional angles are opposite to those in BN52021 and BN52022, but their respective absolute values are rather similar. The modifications in ring *A* and *F* are the result of the changed substitution on C(1): H in BN52020 instead of OH. There is indeed an intramolecular hydrogen bond O3H···O(1) in BN52021 and BN52022 which is no longer possible in BN52020. Cremer & Pople (1975) puckering parameters calculated with the program *PUCK*2 (Luger & Bülow, 1983) show that rings *A* and *F* of BN52020 have a near-twist conformation [$Q_A = 0{\cdot}266\ (4)$ Å, $\varphi_A = 60\ (1)°$, $Q_F = 0{\cdot}295\ (4)$ Å, $\varphi_F = 205\ (1)°$], *B* and *C* are twist [$Q_B = 0{\cdot}417\ (5)$ Å, $\varphi_B = 91\ (1)°$, $Q_C = 0{\cdot}327\ (4)$ Å, $\varphi_C = 19\ (1)°$], *D* is nearly envelope [$Q_D = 0{\cdot}251\ (4)$ Å, $\varphi_D = 247\ (1)°$] and *E* is envelope [$Q_E = 0{\cdot}120\ (4)$ Å, $\varphi_E = 180\ (2)°$]. The

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

BN52020					
C2—C1	1·514 (6)		C10—C9	1·530 (6)	
C5—C1	1·560 (6)		C12—C9	1·538 (6)	
C3—C2	1·528 (6)		C11—C10	1·517 (6)	
O10—C2	1·454 (5)		O(3)—C10	1·399 (5)	
C4—C3	1·552 (5)		O4—C11	1·194 (5)	
C14—C3	1·531 (6)		O5—C11	1·358 (5)	
O2—C3	1·410 (5)		O5—C12	1·441 (5)	
C5—C4	1·522 (6)		O6—C12	1·410 (5)	
C13—C4	1·513 (6)		O7—C13	1·341 (6)	
O6—C4	1·441 (5)		O8—C13	1·208 (6)	
C6—C5	1·548 (6)		C15—C14	1·517 (7)	
C9—C5	1·561 (6)		C16—C14	1·526 (7)	
C7—C6	1·518 (6)		O9—C15	1·207 (5)	
O7—C6	1·469 (6)		O10—C15	1·348 (5)	
C8—C7	1·520 (6)		C18—C17	1·532 (6)	
C9—C8	1·571 (5)		C19—C17	1·543 (7)	
C17—C8	1·582 (6)		C20—C17	1·523 (7)	
BN52022	Molecule *A*	Molecule *B*	BN52022	Molecule *A*	Molecule *B*
C2—C1	1·522 (8)	1·505 (8)	C17—C8	1·551 (8)	1·540 (8)
C5—C1	1·527 (7)	1·514 (8)	C10—C9	1·528 (9)	1·506 (10)
O1—C1	1·386 (9)	1·429 (9)	C12—C9	1·572 (10)	1·530 (10)
C3—C2	1·556 (11)	1·532 (10)	C11—C10	1·525 (10)	1·531 (10)
O10—C2	1·449 (8)	1·453 (7)	O3—C10	1·399 (9)	1·412 (10)
C4—C3	1·580 (8)	1·529 (10)	O4—C11	1·186 (9)	1·161 (10)
C14—C3	1·548 (10)	1·562 (7)	O5—C11	1·357 (9)	1·398 (10)
O2—C3	1·412 (8)	1·420 (8)	O5—C12	1·466 (8)	1·445 (8)
C5—C4	1·556 (10)	1·526 (9)	O6—C12	1·396 (7)	1·413 (8)
C13—C4	1·486 (10)	1·531 (9)	O7—C13	1·357 (10)	1·347 (9)
O6—C4	1·436 (8)	1·441 (9)	O8—C13	1·214 (10)	1·202 (9)
C6—C5	1·537 (10)	1·542 (9)	C15—C14	1·490 (9)	1·520 (12)
C9—C5	1·588 (7)	1·573 (8)	C16—C14	1·505 (12)	1·576 (13)
C7—C6	1·535 (8)	1·486 (7)	O9—C15	1·235 (9)	1·202 (10)
O7—C6	1·476 (9)	1·479 (8)	O10—C15	1·327 (10)	1·375 (12)
C8—C7	1·517 (10)	1·572 (10)	C18—C17	1·588 (12)	1·523 (13)
O11—C7	1·425 (9)	1·362 (8)	C19—C17	1·512 (13)	1·544 (12)
C9—C8	1·547 (9)	1·604 (8)	C20—C17	1·535 (12)	1·491 (11)
Ethanol					
C102—C101	1·408 (17)	1·365 (26)	O102—C102	1·390 (14)	1·394 (19)

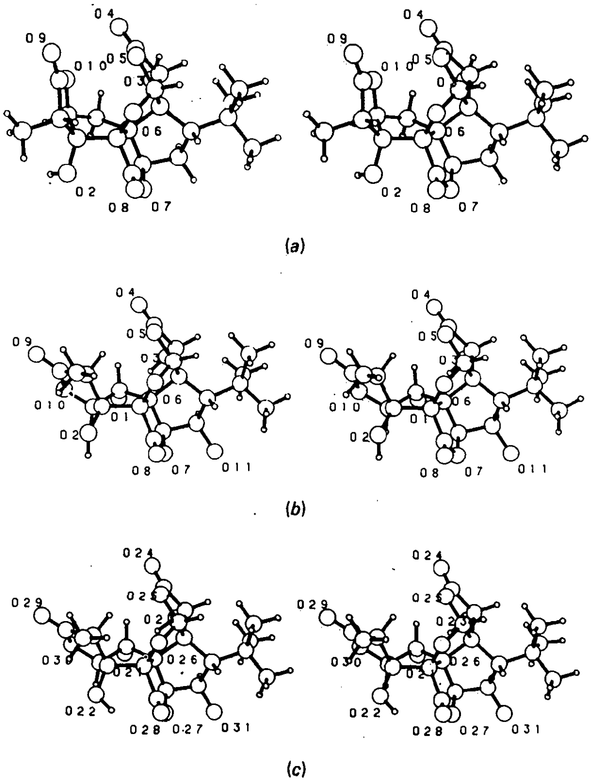

Fig. 2. Stereoscopic views of (*a*) BN52020, (*b*) BN52022, molecule *A* (atoms HO1 and HO7 could not be placed) and (c) BN52022, molecule *B*.

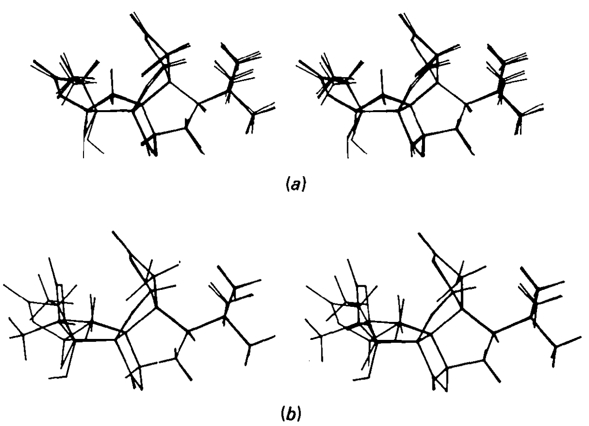

Fig. 3. (*a*) Stereoscopic view of the best molecular fit of BN52021 *A*, *B*, BN52022 *A* and *B*. (*b*) Stereoscopic view of BN52021 (molecule *A*) and BN52020 when rings *B*, *C*, *D* and *E* are fitted.

twist conformation (C_2 symmetry) is characterized by $\varphi = 18,54, \ldots°$, and the envelope (C_s symmetry) by $\varphi = 0,36, \ldots°$. A typical Q value is 0·35 Å in the furanoid ring of sucrose (Brown & Levy, 1973). In the same way, it can be shown that the conformation of the rings in BN52022 are nearly the same as in BN52021, except that the ring *C* of BN52022 *B* is almost an envelope, ring *E* is intermediate between twist and envelope in BN52022 *A*, and envelope in BN52022 *B*; ring *F* has an intermediate conformation in BN52022 *B*.

The crystal of BN52020 contains van der Waals interactions and four hydrogen bonds: O2H···O100 (−*x*, 0·5+*y*, −1·5−*z*), 2·712 (6) Å, O3H···O100 (1−*x*, 0·5+*y*, −1·5−*z*), 2·774 (6) Å, O8···HO100 [*x*, 1+*y*, *z*], 2·865 (6) Å and O9···HO100 (−0·5−*x*, −1−*y*, 0·5+*z*), 2·726 Å. The distance O4···O10 (−0·5+*x*, −0·5−*y*, 1−*z*), 2·859 (6) Å is also significantly shorter than the sum of two oxygen van der Waals radii, currently about 3·0 Å. According to Nyburg & Faerman (1985), O4 linked to a single carbon atom by a double bond should have a spherical shape with a radius of 1·54 Å. So the possibility of a non-spherical shape for O(10) in this lactone can be inferred. In the crystal of BN52022, there is a rather complex network of hydrogen bonds involving ethanol and water molecules. Only some C—OH···O angles and OH···O distances are consistent with linear hydrogen bonds: the H included in O22H···O28 and O2H···O202. O23H···O21 and O3H···O1 are intramolecular hydrogen bonds. The other —OH groups participate in bifurcated hydrogen bonds, but it was not possible to identify their hydrogen positions.

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Crystallographic Studies and Physicochemical Properties of π-Electron Systems. XVI. The Structure of *N*,*N*-Diethyl-3,4-dinitroaniline: Non-Additivity of Substituent Effect on the Geometry of the Benzene Ring

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Abstract. $C_{10}H_{13}N_3O_4$, $M_r = 239·23$, monoclinic, $P2_1/c$, $a = 14·379$ (2), $b = 9·814$ (1), $c = 17·793$ (2) Å, $\beta = 109·71$ (1)°, $V = 2363·9$ (5) Å^3, $Z = 8$, $D_m = 1·330$, $D_x = 1·344$ (10) g cm^{-3}; $\lambda(\mathrm{Cu}\ K\alpha) = 1·54178$ Å, $\mu = 9·63$ cm^{-1}, $F(000) = 1008$, room temperature. Final $R = 0·0479$, $wR = 0·048$ for 2443 counter intensities. The mean e.s.d.'s for bond lengths between heavy atoms are 0·004–0·009 Å and 0·25° for valence angles. Non-additivity of valence angles has been studied by the use of the substituent angular parameters of Domenicano & Murray-Rust [*Tetrahedron Lett.* (1979), **24**, 2283–2286] and Norrestam &

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