## Studies on the Constituents of Atractylodes lancea

Shoji Yahara,<sup>a</sup> Tomoko Higashi,<sup>a</sup> Kazue Iwaki,<sup>a</sup> Toshihiro Nohara\*,<sup>a</sup> Nobuhiro Marubayashi,<sup>b</sup> Ikuhiko Ueda,<sup>b</sup> Hiroshi Kohda,<sup>c</sup> Katsumi Goto,<sup>d</sup> Hiromasa Izumi,<sup>e</sup> Mariko Nuno,<sup>f</sup> Shigeki Katsuki,<sup>g</sup> Susumu Isoda,<sup>h</sup> and Motoyoshi Satake<sup>i</sup>

Faculty of Pharmaceutical Sciences, Kumamoto University, <sup>a</sup> 5–1 Oe-honmachi, Kumamoto 862, Japan, Yoshitomi Pharmaceutical Co., Ltd., <sup>b</sup> Yoshitomicho, Chikujyo-gun, Fukuoka 871, Japan, Hiroshima University School of Medicine, <sup>c</sup> Kasumi 1–2–3, Minami-ku, Hiroshima 734, Japan, Kyoto Pharmaceutical University, <sup>d</sup> Hinobayashi 39, Fushimi-ku, Kyoto 601–13, Japan, Tokyo College of Pharmacy, <sup>e</sup> Horinouchi 1432–1, Hachioji, Tokyo 192–03, Japan, Faculty of Pharmaceutical Sciences, Teikyo University, <sup>f</sup> Suarashi 1091–1, Sagamiko-cho, Kanagawa 199–01, Japan, School of Pharmaceutical Sciences, Kitasato University, <sup>g</sup> Kitasato 2–15–1, Sagamihara, Kanagawa 228, Japan, Showa University, <sup>h</sup> Kamiyoshida 4562, Fujiyoshida, Yamanashi 403, Japan, and National Institute of Hygienic Sciences, <sup>i</sup> Tsukuba Medicinal Plant Research Station, Hachimandai 1, Yatabe-cho, Tsukuba, Ibaraki 305, Japan. Received March 31, 1989

From the polar portion of the methanolic extract of the fresh rhizomes of *Atractylodes lancea* DC., nine new sesquiterpene glycosides [two guaiane-type glycosides, atractylosides A and B (1 and 2), and seven eudesmane-type glycosides, atractylosides C, D, E, F, G, H and I (3—9)] were obtained and their structures were characterized by enzymatic hydrolysis, spectroscopic means and X-ray analysis.

**Keywords** Atractylodes lancea; Compositae; sesquiterpene glycoside; guaiane type; eudesmane type; atractyloside; X-ray analysis

The rhizomes (Japanese name: Jutsu) of Atractylodes plants (Compositae) are an important crude drug used for regulation of body water (Kusuizai) and as a stomachic. Crude drugs derived from plants of this genus include Atractylodis Lanceae Rhizoma (Atractylodes lancea DC. or its varieties: 蒼朮 Changzhu) and Atractylodis Rhizoma (A. japonica KOIDZUMI or A. ovata DC.: 白朮 Baizhu). With regard to the ingredients of these crude drugs, the essential oils such as attractylon, hinesol and  $\beta$ eudesmol are known, but the constituents in the polar portion of the methanolic extract of A. lancea have not yet been surveyed. We have now obtained nine new sesquiterpene glycosides together with syringin and tryptophan. This paper deals with the structural characterization of these new sesquiterpene glycosides of guaiane type, atractylosides A (1) and B (2), and of eudesmane type, atractylosides C, D, E, F, G, H and I (3—9).

Guaiane-Type Glycosides Atractyloside A (1), colorless needles, mp 227—230 °C,  $[\alpha]_D + 20.0^\circ$ , showed a cluster ion peak  $[M+H]^+$ , at m/z 449 in the positive fast atom bombardment mass spectrometry (FAB-MS) and absorption bands due to a five-membered ring ketone at 1740 cm<sup>-1</sup>. The carbon-13 nuclear magnetic resonance ( $^{13}$ C-NMR; Table I) exhibited fifteen carbon signals due to three methyls, four methylenes, three methines, four oxygenated carbons (s × 3 and t × 1) and one carbonyl group along with signals due to the  $\beta$ -D-glucopyranosyl residue (C-1'—C-6',  $\delta$  96.5, 73.6, 76.5, 70.1, 75.8, 61.1). The  $^{1}$ H- $^{1}$ H shift-correlated spectrum (COSY) and  $^{1}$ H- $^{13}$ C COSY of 1

suggested the presence of a sequence of a  $-CH_2-CH_2$ 

CH<sub>2</sub>–CH–CH<sub>2</sub>– in the molecule and enabled us to assign the respective <sup>1</sup>H signals. This result also implied that 1 should be a sesquiterpene glycoside of guaiane type. The ring juncture was supposed to be *trans* from the coupling constant ( $J=11\,\text{Hz}$ ) between H-1 and H-5. On enzymatic hydrolysis 1 provided an aglycone (1a) and D-glucose. In the <sup>13</sup>C-NMR spectrum of 1, signals due to two methyl groups at  $\delta$  23.2 and 23.5 were shifted by -4.2 and -4.7 ppm and a signal due to the carbon bearing a tertiary

hydroxyl group at  $\delta$  80.5 was shifted by +7.8 ppm by comparison with those of 1a, suggesting that the glucosyl moiety should be linked to the tert-hydroxyl group.1) Oxidative ring-fission of 1 with m-chloroperbenzoic acid yielded a product (1b), whose proton nuclear magnetic resonance (1H-NMR) and 13C-NMR spectra showed a methyl ketone signal at  $\delta$  2.28 (3H, s), and signals due to a carbonyl and a carboxyl groups at  $\delta$  210.1 and 176.0, suggesting the occurrence of a 3-keto-4-hydroxyl partial structure in 1. Therefore, the structure of 1 was deduced to be 1,5-trans-4,10,11,14-tetrahydroxyguaian-3-one 11-O-β-D-glucopyranoside. In order to verify this putative structure and determine the configurations, a single crystal of 1 was subjected to the X-ray analysis. Crystal data: C<sub>21</sub>H<sub>36</sub>O<sub>10</sub>; orthorhombic  $P2_12_1$ ; a = 17.433 (4), b = 19.447 (4), c =6.347 (1) Å; V = 2151.7 (7) Å<sup>3</sup>; Z = 4. All unique diffraction maxima with  $2\theta < 120^{\circ}$  were collected on a four-circle diffractometer using graphite-monochromated  $CuK_{\alpha}$  ( $\lambda =$ 

TABLE I. <sup>13</sup>C-NMR Data for 1, 1a and 2 (in Pyridine- $d_5$ )

|        | _ 1   | 1a    | 2    |
|--------|-------|-------|------|
| C-1    | 42.1  | 43.6  | 44.0 |
| C-2    | 34.8  | 35.9  | 37.9 |
| C-3    | 221.4 | 220.6 | 79.7 |
| C-4    | 74.2  | 74.3  | 75.8 |
| C-5    | 45.4  | 46.5  | 58.5 |
| C-6    | 28.5  | 28.1  | 31.1 |
| C-7    | 47.3  | 51.0  | 45.9 |
| C-8    | 21.7  | 28.7  | 24.4 |
| C-9    | 34.3  | 30.1  | 31.9 |
| C-10   | 81.5  | 81.0  | 81.3 |
| C-11   | 80.5  | 72.7  | 80.7 |
| C-12   | 23.2  | 27.4  | 24.1 |
| C-13   | 23.5  | 28.2  | 25.0 |
| C-14   | 68.4  | 70.1  | 68.€ |
| C-15   | 17.6  | 19.1  | 16.0 |
| Glc-1' | 96.5  |       | 98.6 |
| Glc-2' | 73.6  |       | 75.3 |
| Glc-3' | 76.5  | •     | 78.8 |
| Glc-4' | 70.1  |       | 71.8 |
| Glc-5' | 75.8  |       | 78.1 |
| Glc-6' | 61.1  |       | 62.8 |

2996 Vol. 37, No. 11

Table II. Atomic Coordinates ( $\times 10^4$  or  $10^3$ ) and Equivalent Isotropic Temperature Factors ( $\mathring{A}^2 \times 10^2$ ) with Their e.s.d. Values in Parentheses for

| Atom $x$ $y$ $z$ $B_{eq}$ O3 5595 (1) 4065 (1) 4095 (5) 3.89 (6)  O4 4778 (1) 2849 (1) 5593 (4) 2.64 (5)  O10 7031 (1) 1799 (1) 1793 (4) 2.81 (5)  O11 5079 (1) 503 (1) 6949 (3) 1.97 (4)  O14 8607 (1) 2059 (1) 1612 (4) 2.76 (5)  C1 6848 (1) 2620 (1) 4598 (5) 1.84 (6)  C2 6627 (2) 3264 (1) 3319 (5) 2.49 (6)  C3 5892 (2) 3508 (1) 4337 (5) 2.23 (6)  C4 5584 (2) 2943 (1) 5811 (5) 2.01 (6)  C5 6056 (1) 2307 (1) 5150 (5) 1.84 (6)  C7 6286 (1) 1024 (1) 5694 (5) 2.07 (6)  C8 7170 (2) 924 (2) 5456 (6) 2.94 (7)  C9 7668 (2) 1568 (2) 5179 (5) 2.47 (7)  C10 7408 (2) 2115 (1) 3578 (5) 2.05 (6)  C11 5922 (1) 400 (1) 6843 (5) 2.15 (6)  C12 6100 (2) -275 (1) 5720 (7) 3.26 (8)  C13 6127 (2) 349 (2) 9167 (6) 3.10 (7)  C14 8099 (2) 2514 (2) 2730 (6) 2.60 (7)  O1' 4701 (1) 1096 (1) 3999 (3) 2.17 (4)  O2' 3731 (1) -242 (1) 7005 (4) 2.53 (4)  O4' 2951 (1) 312 (1) 4681 (3) 2.46 (4)  O4' 2951 (1) 312 (1) 4681 (3) 2.46 (4)  O4' 2951 (1) 312 (1) 4681 (3) 2.46 (4)  O4' 2951 (1) 1024 (1) 512 (5) (4) 2.53 (4)  O4' 2951 (1) 1024 (1) 512 (5) 1.95 (6)  C1' 4640 (2) 464 (1) 5121 (5) 1.92 (6)  C3' 3391 (1) 221 (1) 400 (1) 6813 (3) 2.46 (4)  O4' 2951 (1) 1024 (1) 782 (4) 3.07 (5) 2.56 (7)  O1' 4701 (1) 1096 (1) 3999 (3) 2.17 (4)  O2' 3731 (1) -242 (1) 7005 (4) 2.53 (4)  O3' 2514 (1) 312 (1) 4681 (3) 2.46 (4)  O4' 2951 (1) 1024 (1) 782 (4) 3.07 (5) 2.56 (7)  O1' 4600 (2) 464 (1) 5121 (5) 1.92 (6)  C5' 4465 (2) 1074 (1) 2646 (5) 1.89 (6)  C6' 4465 (2) 1074 (1) 2076 (5) 2.01 (6)  C6' 4465 (2) 1074 (1) 2076 (5) 2.01 (6)  C6' 4465 (2) 1074 (1) 2076 (5) 2.01 (6)  C6' 4465 (2) 1074 (1) 2076 (5) 2.01 (6)  C6' 4465 (2) 1074 (1) 2076 (5) 2.01 (6)  C6' 4465 (2) 1074 (1) 2076 (5) 2.01 (6)  C6' 4465 (2) 1074 (1) 2076 (5) 2.01 (6)  C6' 4465 (2) 1074 (1) 2076 (5) 2.01 (6)  C6' 4465 (2) 1074 (1) 2076 (5) 2.01 (6)  C6' 4465 (2) 1074 (1) 2076 (5) 2.01 (6)  C6' 4465 (2) 1074 (1) 2076 (5) 2.01 (6)  C6' 4465 (2) 1074 (1) 2076 (5) 2.01 (6)  C6' 4465 (2) 1074 (1) 2076 (5) 2.01 (6)  C6' 4465 (2) 1074 (1) 2076 (5) 2.01 (6)  C6' 4465 (2) 1074 (1) 2076 (5) 2.00 (6)  C6'    |       |          |          |          |             |
|--|-------|----------|----------|----------|-------------|
| O4   | Atom  | x        | у        | z        | $B_{ m eq}$ |
| O4   | 03    | 5595 (1) | 4065 (1) | 4095 (5) | 3.89 (6)    |
| O10 7031 (I) 1799 (I) 1793 (4) 2.81 (S) O11 5079 (I) 503 (I) 6549 (3) 1.97 (4) O14 8607 (I) 2059 (I) 1612 (4) 2.76 (S) C1 6848 (I) 2620 (I) 4598 (S) 1.84 (6) C2 6627 (2) 3264 (I) 3319 (S) 2.49 (6) C3 5892 (2) 33508 (I) 4337 (S) 2.23 (6) C4 5584 (2) 2943 (I) 5811 (S) 2.01 (6) C5 6056 (I) 2307 (I) 5150 (S) 1.84 (6) C6 6052 (2) 1710 (I) 6724 (S) 1.96 (6) C7 6286 (I) 1024 (I) 5694 (S) 2.07 (6) C8 7170 (2) 924 (2) 5456 (6) 2.94 (7) C10 7408 (2) 2115 (I) 3578 (S) 2.05 (6) C11 6100 (2) -275 (I) 5720 (7) 3.26 (8) C13 6127 (2) 349 (2) 9167 (6) 3.10 (7) C14 8099 (2) 2514 (2) 2730 (6) 2.60 (7) C15 5718 (2) 3167 (2) 8077 (S) 2.56 (7) O1' 4701 (I) 1096 (I) 3999 (3) 2.17 (4) O3' 2514 (I) 312 (I) 4681 (3) 2.46 (4) O4' 2951 (I) 1024 (I) 582 (4) 307 (S) C1' 4640 (2) 464 (I) 5121 (S) 1.92 (6) C1' 4640 (2) 464 (I) 5121 (S) 1.92 (6) C1' 4640 (2) 464 (I) 522 (I) 533 (S) 2.95 (G) C1' 4640 (2) 464 (I) 522 (I) 524 (S) 1.84 (G) C3' 3291 (I) 362 (I) 3931 (S) 1.84 (G) C4' 3410 (2) 1014 (I) 2646 (S) 1.89 (G) C6' 4465 (2) 1714 (I) 862 (S) 2.46 (G) C1' 4640 (2) 464 (I) 5121 (S) 1.92 (G) C1' 4660 (2) 1714 (I) 862 (S) 2.46 (G) C1' 4665 (2) 1714 (I) 862 (S) 2.46 (G) C1' 4660 (2) 464 (I) 5121 (S) 1.92 (G) C1' 4640 (2) 464 (I) 5121 (S) 1.92 (G) C1' 4640 (2) 464 (I) 5121 (S) 1.92 (G) C1' 4640 (2) 464 (I) 5121 (S) 1.92 (G) C1' 4640 (2) 464 (I) 5121 (S) 1.92 (G) C1' 4660 (2) 1714 (I) 862 (S) 2.46 (G) HC1 711 (2) 279 (2) 606 (S) 2.60 (O) HC2 636 (2) 181 (I) 800 (S) 2.2 (0.6) HC3 738 (2) 138 (2) 473 (6) 3.5 (O.7) H1C8 727 (2) 58 (2) 165 (I) 707 (F) 70.99 H2C2 707 (2) 367 (2) 332 (6) 4.2 (0.8) HC1 711 (2) 279 (2) 606 (S) 2.6 (O.7) H1C8 727 (2) 58 (2) 165 (I) 707 (F) 70.99 H2C1 577 (2) 367 (2) 332 (G) 4.2 (0.8) HC1 71 (I) 800 (2) 79 (2) 992 (7) 4.5 (0.9) H1C1 481 (2) 4 (2) 403 (S) 2.9 (O.7) H1C2 657 (2) 360 (2) 79 (2) 992 (7) 4.5 (0.9) H1C1 481 (2) 4 (2) 403 (S) 2.9 (O.7) H1C2 540 (2) 363 (G) 30 (O.7) H2C3 738 (2) 174 (G) 3.7 (O.9) H2C4 334 (2) -12 (2) 79 (1) (7) 4.7 (0.9) H2C6 422 (2) 165 (2) -57 (7) 3.9 (0.8) H2C6 422 (2) 165 (2) -57 (7) 3.9 (0.8) H2 |       | ` '      | ` '      | , ,      |             |
| O11  |       |          | , ,      |          |             |
| O14 8607 (I) 2059 (I) 1612 (4) 2.76 (5) C1 6848 (I) 2620 (I) 4598 (S) 1.84 (6) C2 6627 (2) 3264 (I) 3319 (5) 2.49 (6) C3 5892 (2) 3508 (I) 4337 (5) 2.23 (6) C4 5584 (2) 2943 (I) 5811 (5) 2.01 (6) C5 6056 (I) 2307 (I) 5150 (5) 1.84 (6) C6 6052 (2) 1710 (I) 6724 (5) 1.96 (6) C7 6286 (I) 1024 (I) 5694 (5) 2.07 (6) C8 7170 (2) 924 (2) 5456 (6) 2.94 (7) C10 7408 (2) 2115 (I) 3578 (5) 2.25 (6) C10 7408 (2) 2115 (I) 3578 (5) 2.05 (6) C11 5922 (I) 400 (I) 6843 (5) 2.15 (6) C12 6100 (2) -275 (I) 5720 (7) 3.26 (8) C13 6127 (2) 349 (2) 9167 (6) 3.10 (7) C15 5718 (2) 3167 (2) 8077 (5) 2.56 (7) O1' 4701 (I) 1096 (I) 3999 (3) 2.17 (4) O2' 3731 (I) -242 (I) 7005 (4) 2.53 (4) O4' 2951 (I) 312 (I) 4681 (3) 2.46 (4) O4' 2951 (I) 312 (I) 4681 (3) 2.46 (4) O4' 2951 (I) 312 (I) 4681 (3) 2.46 (4) O4' 2951 (I) 312 (I) 4681 (3) 2.46 (4) O4' 2951 (I) 312 (I) 4681 (3) 2.46 (4) O4' 2951 (I) 312 (I) 4681 (3) 2.46 (4) O4' 2951 (I) 312 (I) 4681 (3) 2.46 (4) O4' 2951 (I) 312 (I) 4681 (3) 2.46 (4) O4' 2951 (I) 312 (I) 524  |       |          |          | , ,      |             |
| C1 6848 (I) 2620 (I) 4598 (5) 1.84 (6) C2 6667 (2) 3264 (I) 3319 (5) 2.49 (6) C3 5892 (2) 3508 (I) 4337 (5) 2.23 (6) C4 5584 (2) 2943 (I) 5811 (5) 2.01 (6) C5 6056 (I) 2307 (I) 5150 (5) 1.84 (6) C7 6286 (I) 1024 (I) 5694 (5) 2.07 (6) C8 7170 (2) 924 (2) 5456 (6) 2.94 (7) C9 7668 (2) 1568 (2) 5179 (5) 2.47 (7) C10 7408 (2) 2115 (I) 3578 (5) 2.05 (6) C11 5922 (I) 400 (I) 6843 (5) 2.15 (6) C12 6100 (2) -275 (I) 5720 (7) 3.26 (8) C13 6127 (2) 349 (2) 9167 (6) 3.10 (7) C14 8099 (2) 2514 (2) 2730 (6) 2.60 (7) C15 5718 (2) 3167 (2) 8077 (5) 2.56 (7) O1' 4701 (I) 1096 (I) 3999 (3) 2.17 (4) O2' 3731 (I) -242 (I) 7005 (4) 2.53 (4) O4' 2951 (I) 312 (I) 4681 (3) 2.46 (4) O4' 2951 (I) 1024 (I) 782 (4) 3.07 (5) C1' 4640 (2) 464 (I) 5121 (5) 1.84 (6) C3' 3291 (I) 362 (I) 3931 (5) 1.92 (6) C4' 3410 (2) 1014 (I) 2076 (5) 2.01 (6) C6' 4265 (2) 1074 (I) 2076 (5) 2.01 (6) C6' 4465 (2) 1714 (I) 862 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.46 (6) HC2 707 (2) 367 (2) 332 (6) 42 (0.8) HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C6 552 (2) 165 (1) 726 (5) 1.5 (0.6) H2C6 636 (2) 181 (I) 800 (5) 2.2 (0.6) H1C9 773 (2) 184 (2) 299 (2) 363 (6) 3.0 (0.7) H1C1 771 (2) 279 (2) 606 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.01 (6) HC6 552 (2) 165 (1) 726 (5) 1.5 (0.6) H1C9 773 (2) 184 (2) 582 (2) 415 (6) 3.5 (0.7) H2C9 821 (2) 138 (2) 473 (6) 3.5 (0.7) H2C9 821 (2) 138 (2) 473 (6) 3.5 (0.8) H1C1 771 (2) 279 (2) 58 (2) 415 (6) 3.5 (0.7) H2C2 707 (2) 367 (2) 332 (6) 4.2 (0.8) H1C9 773 (2) 184 (2) 582 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 991 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 991 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 991 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 991 (7) 4.5 (0.9) H3C15 584 (2) 277 (2) 992 (7) 4.5 (0.9) H3C15 584 (2) 277 (2) 992 (7) 4.5 (0.9) H3C15 584 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 584 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 586 (2) 791 (1) 695 (5) 2.0 (0.6) H3C16 442 (2) 165 (2) -57 (7) 3.9 (0.8) H3C15 580 (2) 776 (4) 22 (2) 410 (6) 20 (7) H3C16 442 (2) 165 (2) -57 (7) 3.9 (0.8) H3C15 540 (2)  |       | ` '      |          |          |             |
| C2 6627 (2) 3264 (1) 3319 (5) 2.49 (6) C3 5892 (2) 3508 (1) 4337 (5) 2.23 (6) C4 5584 (2) 2943 (1) 5811 (5) 2.01 (6) C5 6056 (1) 2307 (1) 5150 (5) 1.84 (6) C5 6052 (2) 1710 (1) 6724 (5) 1.96 (6) C7 6286 (1) 1024 (1) 5694 (5) 2.07 (6) C8 7170 (2) 924 (2) 5456 (6) 2.94 (7) C9 7668 (2) 1568 (2) 5179 (5) 2.47 (7) C10 7408 (2) 2115 (1) 3578 (5) 2.15 (6) C11 5922 (1) 400 (1) 6843 (5) 2.15 (6) C12 6100 (2) -275 (1) 5720 (7) 3.26 (8) C13 6127 (2) 349 (2) 947 (2) 2514 (2) 2730 (6) 2.60 (7) C15 5718 (2) 3167 (2) 8077 (5) 2.56 (7) O1′ 4701 (1) 1096 (1) 3999 (3) 2.17 (4) O2′ 3731 (1) -242 (1) 7005 (4) 2.53 (4) O3′ 2514 (1) 312 (1) 4681 (3) 2.46 (4) O4′ 2951 (1) 1024 (1) 782 (4) 3.07 (5) C1′ 4640 (2) 464 (1) 5121 (5) 1.92 (6) C2′ 3811 (2) 384 (1) 5864 (5) 1.84 (6) C3′ 3291 (1) 362 (1) 3931 (5) 1.92 (6) C4′ 3410 (2) 1014 (1) 2646 (5) 1.89 (6) C4′ 3410 (2) 1014 (1) 2646 (5) 1.89 (6) C4′ 3410 (2) 1014 (1) 2646 (5) 1.89 (6) C4′ 3410 (2) 1014 (1) 2646 (5) 1.89 (6) C6′ 4265 (2) 1074 (1) 2076 (5) 2.60 (7) H2C2 707 (2) 367 (2) 337 (2) 174 (1) 2076 (5) 2.60 (7) C1′ 4640 (2) 464 (1) 5121 (5) 1.92 (6) C5′ 4265 (2) 1074 (1) 2076 (5) 2.61 (6) C4′ 3410 (2) 1014 (1) 2646 (5) 1.89 (6) C6′ 4465 (2) 1714 (1) 862 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.6 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) (4) H2C2 707 (2) 367 (2) 332 (6) 4.2 (0.8) HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C6 552 (2) 165 (1) 726 (5) 1.5 (0.6) H2C6 636 (2) 181 (1) 800 (5) 2.2 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C2 577 (2) 367 (2) 332 (6) 4.2 (0.8) H1C1 667 (2) -42 (2) 580 (6) 3.0 (0.7) H1C1 360 (2) 22 (2) 941 (7) 4.7 (0.9) H1C1 360 (2) 22 (2) 941 (7) 4.7 (0.9) H1C1 470 (2) 279 (2) 580 (6) 3.0 (0.7) H1C1 360 (2) 27 (2) 363 (6) 3.0 (0.7) H1C1 360 (2) 27 (2) 360 (3) (3) (3) (0.7) H1C1 360 (2) 27 (2) 360 (3) (3) (3) (0.7) H1C1 360 (2) 27 (2) 360 (3) (3) (3) (0.7) H1C1 360 (2) 27 (2) 390 (6) 2.5 (0.7) H1C1 360 (2) 27 (2) 390 (6) 2.5 (0.7) H1C1 360 (2) 27 (2) 390 (6) 2.5 (0.7) H1C1 360 (2) 27 (2) 390 (6) 2.5 (0.7) H1C1 360 (2 | C1    |          |          |          |             |
| C4   | C2    | 6627 (2) |          | 3319 (5) | 2.49 (6)    |
| C5 6056 (1) 2307 (1) 5150 (5) 1.84 (6) C6 6052 (2) 1710 (1) 6724 (5) 1.96 (6) C7 6286 (1) 1024 (1) 5694 (5) 2.07 (6) C8 7170 (2) 924 (2) 5456 (6) 2.94 (7) C9 7668 (2) 1568 (2) 5179 (5) 2.47 (7) C10 7408 (2) 2115 (1) 3578 (5) 2.05 (6) C11 5922 (1) 400 (1) 6843 (5) 2.15 (6) C12 6100 (2) -275 (1) 5720 (7) 3.26 (8) C13 6127 (2) 349 (2) 9167 (6) 3.10 (7) C14 8099 (2) 2514 (2) 2730 (6) 2.60 (7) C15 5718 (2) 3167 (2) 8077 (5) 2.56 (7) O1' 4701 (1) 1096 (1) 3999 (3) 2.17 (4) O3' 2514 (1) 312 (1) 4681 (3) 2.46 (4) O4' 2951 (1) 1024 (1) 782 (4) 3.07 (5) C1' 4640 (2) 464 (1) 5121 (5) 1.92 (6) C2' 3811 (2) 384 (1) 5864 (5) 1.84 (6) C3' 3291 (1) 362 (1) 3931 (5) 1.92 (6) C5' 4265 (2) 1074 (1) 2076 (5) 2.01 (6) C6' 4465 (2) 1014 (1) 2646 (5) 1.89 (6) C5' 4265 (2) 1074 (1) 2076 (5) 2.01 (6) C6' 4465 (2) 1714 (1) 862 (5) 2.66 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) HC2 (7) C1 (1) 279 (2) 606 (5) 2.66 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) H1C8 727 (2) 367 (2) 332 (6) 4.2 (0.8) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) H1C6 552 (2) 165 (1) 726 (5) 2.01 (6) 4.00 (7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H1C9 733 (2) 184 (2) 652 (2) 992 (7) 4.5 (0.9) H1C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H1C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H1C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H1C14 794 (2) 293 (2) 138 (2) 473 (6) 3.5 (0.7) H1C14 794 (2) 293 (2) 138 (2) 473 (6) 3.5 (0.7) H1C14 794 (2) 293 (2) 174 (1) 5.3 (1.0) H1C14 794 (2) 293 (2) 174 (6) 3.5 (0.7) H1C15 600 (2) 79 (2) 992 (7) 4.5 (0.9) H1C14 794 (2) 293 (2) 174 (6) 3.5 (0.7) H1C15 600 (2) 79 (2) 992 (7) 4.5 (0.9) H1C14 794 (2) 293 (2) 174 (6) 3.5 (0.7) H1C15 600 (2) 79 (2) 992 (7) 4.5 (0.9) H1C14 794 (2) 293 (2) 174 (6) 3.5 (0.7) H1C15 600 (2) 79 (2) 992 (7) 4.5 (0.9) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C14 794 (2) 403 (3) (2) 2.9 (0.7) H1C15 | C3    | 5892 (2) | 3508 (1) | 4337 (5) | 2.23 (6)    |
| C6 6052 (2) 1710 (1) 6724 (5) 1.96 (6) C7 6286 (1) 1024 (1) 5694 (5) 2.07 (6) C8 7170 (2) 924 (2) 5456 (6) 2.94 (7) C9 7668 (2) 1568 (2) 5179 (5) 2.47 (7) C10 7408 (2) 2115 (1) 3578 (5) 2.05 (6) C11 5922 (1) 400 (1) 6843 (5) 2.15 (6) C12 6100 (2) -275 (1) 5720 (7) 3.26 (8) C13 6127 (2) 349 (2) 9167 (6) 3.10 (7) C14 8099 (2) 2514 (2) 2730 (6) 2.60 (7) C15 5718 (2) 3167 (2) 8077 (5) 2.55 (7) O1′ 4701 (1) 1096 (1) 3999 (3) 2.17 (4) O2′ 3731 (1) -242 (1) 7005 (4) 2.53 (4) O4′ 2951 (1) 1024 (1) 782 (4) 3.07 (5) O6′ 4203 (1) 2321 (1) 1902 (4) 2.90 (5) C1′ 4640 (2) 464 (1) 5121 (5) 1.92 (6) C2′ 3811 (2) 384 (1) 5864 (5) 1.84 (6) C3′ 3291 (1) 362 (1) 3931 (5) 1.92 (6) C5′ 4265 (2) 1074 (1) 2646 (5) 1.89 (6) HC1 711 (2) 279 (2) 606 (5) 2.66 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.70 (9) 367 (2) 367 (2) 368 (2) 307 (2) 176 (7) 4.70 (9) H2C2 707 (2) 367 (2) 332 (6) 3.0 (0.7) H1C8 738 (2) 3167 (2) 332 (6) 3.0 (0.7) H1C8 738 (2) 307 (2) 376 (3) 3.0 (0.7) H1C2 666 (2) 1714 (1) 862 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.6 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.70 (9) H2C2 707 (2) 367 (2) 363 (6) 3.0 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C2 707 (2) 367 (2) 367 (2) 332 (6) 4.2 (0.8) HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C2 707 (2) 367 (2) 336 (2) 433 (6) 3.0 (0.7) H1C1 667 (2) 104 (2) 413 (6) 2.9 (0.7) H1C2 667 (2) -42 (2) 58 (6) (6) 3.5 (0.7) H2C2 707 (2) 367 (2) 332 (6) 4.2 (0.8) HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C1 773 (2) 184 (2) 652 (7) 4.6 (0.9) H2C1 577 (2) 58 (2) 415 (6) 3.5 (0.7) H2C2 577 (2) 58 (2) 415 (6) 3.5 (0.7) H2C2 577 (2) 58 (2) 415 (6) 3.5 (0.7) H2C1 57 (2) 58 (2) 415 (6) 3.5 (0.7) H2C1 57 (2) 58 (2) 415 (6) 3.5 (0.7) H2C2 577 (2) 58 (2) 415 (6) 3.5 (0.7) H2C1 57 (2) 58 (2) 415 (6) 3.5 (0.7) H2C1 57 (2) 58 (2) 415 (6) 3.5 (0.7) H2C1 57 (2) 58 (2) 415 (6) 3.5 (0.7) H2C1 570 (2) 58 (2) 415 (6) 3.5 (0.7) H2C1 570 (2) 58 (2) 415 (6) 3.5 (0.7) H2C1 570 (2) 58 (2) 415 (6) 3.5 (0.7) H2C1 570 (2) 58 (2) 415 (6) 3.5 (0.7) H2C1 570 (2) 58 (2) 415 (6) 3.5 (0.7) H2C1 57 |       | 5584 (2) |          | 5811 (5) | 2.01 (6)    |
| C7 6286 (1) 1024 (1) 5694 (5) 2.07 (6) C8 7170 (2) 924 (2) 5456 (6) 2.94 (7) C10 7408 (2) 2115 (1) 3578 (5) 2.47 (7) C10 7408 (2) 2115 (1) 3578 (5) 2.05 (6) C11 5922 (1) 400 (1) 6843 (5) 2.15 (6) C12 6100 (2) -275 (1) 5720 (7) 3.26 (8) C13 6127 (2) 349 (2) 9167 (6) 3.10 (7) C14 8099 (2) 2514 (2) 2730 (6) 2.60 (7) C15 5718 (2) 3167 (2) 8077 (5) 2.56 (7) O1′ 4701 (1) 1096 (1) 3999 (3) 2.17 (4) O2′ 3731 (1) -242 (1) 7005 (4) 2.53 (4) O3′ 2514 (1) 312 (1) 4681 (3) 2.46 (4) O4′ 2951 (1) 1024 (1) 782 (4) 3.07 (5) C1′ 4640 (2) 464 (1) 5121 (5) 1.92 (6) C1′ 4640 (2) 464 (1) 5121 (5) 1.92 (6) C2′ 3811 (2) 384 (1) 5864 (5) 1.84 (6) C3′ 3291 (1) 362 (1) 3931 (5) 1.92 (6) C4′ 3410 (2) 1014 (1) 2646 (5) 1.89 (6) C5′ 4265 (2) 1074 (1) 2076 (5) 2.01 (6) HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.70 (9) H2C2 707 (2) 367 (2) 332 (6) 3.0 (0.7) H1C8 727 (2) 58 (2) 165 (1) 726 (5) 1.5 (0.6) H2C9 821 (2) 184 (2) 184 (2) 180 (4) 180 (5) 2.2 (0.6) H1C9 773 (2) 184 (2) 184 (2) 180 (4) 180 (5) 2.2 (0.6) H1C9 773 (2) 184 (2) 180 (4) 299 (7) 415 (6) 3.5 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H1C9 821 (2) 184 (2) 182 (2) 184 (2) 413 (6) 2.9 (0.7) H1C9 773 (2) 184 (2) 182 (2) 184 (2) 180 (5) 2.9 (6) (7) H1C9 773 (2) 184 (2) 180 (3) 3.7 (0.8) H1C12 577 (2) 58 (2) 415 (6) 3.5 (0.7) H1C9 773 (2) 184 (2) 408 (8) 6.6 (1.2) H1C1 711 (2) 279 (2) 992 (7) 4.5 (0.9) H1C9 773 (2) 184 (2) 493 (2) 473 (6) 3.7 (0.8) H1C12 577 (2) 58 (2) 415 (6) 3.5 (0.7) H2C12 577 (2) 69 (2) 693 (6) 2.9 (0.7) H3C13 591 (2) 124 (2) 491 (7) 5.3 (1.0) H2C15 540 (2) 27 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) 174 (6) 3.7 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C15 588 (2) 277 (2) 991 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H1C15 540 (2) 363 (2) 383 (2) 433 (2) 433 (2) 443 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 383 (2) 433 (2) 443 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 383 (2) 433 (3) (2) 90.7 (4) 60.9 H2C15 540 (2) 363 (2) 383 (2) 433 (3) (2) 90.7 (4) 60 |       | ` '      |          | · /      | ` '         |
| C8 7170 (2) 924 (2) 5456 (6) 2.94 (7) C9 7668 (2) 1568 (2) 5179 (5) 2.47 (7) C10 7408 (2) 2115 (1) 3578 (5) 2.05 (6) C11 5922 (1) 400 (1) 6843 (5) 2.15 (6) C12 6100 (2) -275 (1) 5720 (7) 3.26 (8) C13 6127 (2) 349 (2) 9167 (6) 3.10 (7) C14 8099 (2) 2514 (2) 2730 (6) 2.60 (7) C15 5718 (2) 3167 (2) 8077 (5) 2.56 (7) O1′ 4701 (1) 1096 (1) 3999 (3) 2.17 (4) O2′ 3731 (1) -242 (1) 7005 (4) 2.53 (4) O3′ 2514 (1) 312 (1) 4681 (3) 2.46 (4) O4′ 2951 (1) 1024 (1) 782 (4) 3.07 (5) C1′ 4640 (2) 464 (1) 5121 (5) 1.92 (6) C2′ 3811 (2) 384 (1) 5864 (5) 1.84 (6) C3′ 3291 (1) 362 (1) 3931 (5) 1.92 (6) C4′ 3410 (2) 1014 (1) 2646 (5) 1.89 (6) C6′ 4465 (2) 1074 (1) 2076 (5) 2.01 (6) C6′ 4465 (2) 1714 (1) 862 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.60 (7) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) H2C2 707 (2) 367 (2) 332 (6) 3.00 (7) H1C6 552 (2) 165 (1) 726 (5) 1.5 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 145 (6) 3.5 (0.7) H1C9 73 (2) 184 (2) 194 (2) 413 (6) 2.9 (0.7) H1C1 670 (2) 104 (2) 413 (6) 2.9 (0.7) H1C2 653 (2) 165 (1) 726 (5) 1.5 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C2 670 (2) 165 (2) 165 (1) 726 (5) 1.5 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C1 670 (2) 184 (2) 652 (7) 4.6 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H1C1 670 (2) 104 (2) 413 (6) 2.9 (0.7) H1C1 670 (2) 184 (2) 652 (7) 4.6 (0.9) H1C1 670 (2) 104 (2) 413 (6) 3.5 (0.7) H1C1 670 (2) 104 (2) 413 (6) 3.5 (0.7) H1C1 670 (2) 184 (2) 652 (7) 4.6 (0.9) H1C1 670 (2) 184 (2) 652 (7) 4.6 (0.9) H1C1 670 (2) 184 (2) 664 (6) 4.0 (0.9) H1C1 670 (2) 184 (2) 652 (7) 4.6 (0.9) H1C1 670 (2) 184 (2) 652 (7) 4.6 (0.9) H1C1 670 (2) 184 (2) 652 (7) 4.6 (0.9) H1C1 670 (2) 184 (2) 652 (7) 4.6 (0.9) H1C1 670 (2) 184 (2) 652 (7) 4.6 (0.9) H1C1 670 (2) 184 (2) 652 (7) 4.6 (0.9) H1C1 670 (2) 184 (2) 652 (7) 4.6 (0.9) H1C1 670 (2) 184 (2) 652 (7) 4.6 (0.9) H1C1 670 (2) 184 (2) 652 (2) 664 (6) 4.0 (0.9) H1C1 670 (2) 184 (2) 652 (2) 664 (6) 4.0 (0.9) H1C1 670 (2) 184 (2) 652 ( |       |          |          |          |             |
| C9 7668 (2) 1568 (2) 5179 (5) 2.47 (7) C10 7408 (2) 2115 (1) 3578 (5) 2.05 (6) C11 5922 (1) 400 (1) 6843 (5) 2.15 (6) C12 6100 (2) -275 (1) 5720 (7) 3.26 (8) C13 6127 (2) 349 (2) 9167 (6) 3.10 (7) C14 8099 (2) 2514 (2) 2730 (6) 2.60 (7) C15 5718 (2) 3167 (2) 8077 (5) 2.56 (7) O1′ 4701 (1) 1096 (1) 3999 (3) 2.17 (4) O2′ 3731 (1) -242 (1) 7005 (4) 2.53 (4) O3′ 2514 (1) 312 (1) 4681 (3) 2.46 (4) O4′ 2951 (1) 1024 (1) 782 (4) 3.07 (5) C6′ 4203 (1) 2321 (1) 1902 (4) 2.90 (5) C1′ 4640 (2) 464 (1) 5121 (5) 1.92 (6) C2′ 3811 (2) 384 (1) 5864 (5) 1.84 (6) C3′ 3291 (1) 362 (1) 3931 (5) 1.92 (6) C4′ 3410 (2) 1014 (1) 2646 (5) 1.89 (6) C5′ 4265 (2) 1074 (1) 862 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.6 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) H2C2 707 (2) 367 (2) 332 (6) 4.2 (0.8) HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C8 732 (2) 184 (2) 413 (6) 2.9 (7) H1C8 732 (2) 184 (2) 413 (6) 2.9 (7) H1C8 732 (2) 184 (2) 413 (6) 2.9 (0.7) H1C9 733 (2) 176 (7) 4.7 (0.9) H2C9 821 (2) 184 (2) 473 (6) 3.5 (0.7) H1C8 732 (2) 184 (2) 493 (3) (0.7) H1C9 733 (2) 176 (7) 4.7 (0.9) H2C9 821 (2) 184 (2) 652 (7) 4.6 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H2C1 577 (2) 58 (2) 415 (6) 3.5 (0.7) H1C1 733 (2) 184 (2) 652 (7) 4.6 (0.9) H2C2 577 (2) 58 (2) 415 (6) 3.5 (0.7) H2C2 577 (2) 58 (2) 415 (6) 3.5 (0.7) H1C1 733 (2) 184 (2) 652 (7) 4.6 (0.9) H2C1 577 (2) 58 (2) 415 (6) 3.5 (0.7) H1C1 733 (2) 184 (2) 652 (7) 4.6 (0.9) H2C1 577 (2) 60 (3) -31 (2) 408 (8) 6.6 (1.2) H1C1 4794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C1 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C12 600 (3) -31 (2) 408 (8) 6.6 (1.2) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C15 625 (2) 331 (2) 408 (8) 6.6 (1.2) H1C15 625 (2) 331 (2) 408 (8) 6.6 (1.2) H1C15 625 (2) 331 (2) 408 (8) 6.6 (1.2) H1C15 625 (2) 331 (2) 408 (8) 6.6 (1.2) H1C15 625 (2) 331 (2) 408 (3) (3) (0.7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C15 625 ( |       |          |          | ` '      |             |
| C10 7408 (2) 2115 (1) 3578 (5) 2.05 (6) C11 5922 (1) 400 (1) 6843 (5) 2.15 (6) C12 6100 (2) -275 (1) 5720 (7) 3.26 (8) C13 6127 (2) 349 (2) 9167 (6) 3.10 (7) C14 8099 (2) 2514 (2) 2730 (6) 2.60 (7) C15 5718 (2) 3167 (2) 8077 (5) 2.56 (7) O1′ 4701 (1) 1096 (1) 3999 (3) 2.17 (4) O2′ 3731 (1) -242 (1) 7005 (4) 2.53 (4) O3′ 2514 (1) 312 (1) 4681 (3) 2.46 (4) O4′ 2951 (1) 1024 (1) 782 (4) 3.07 (5) C1′ 4640 (2) 464 (1) 5121 (5) 1.92 (6) C2′ 3811 (2) 384 (1) 5864 (5) 1.84 (6) C3′ 3299 (1) 362 (1) 3931 (5) 1.92 (6) C3′ 3410 (2) 1014 (1) 2646 (5) 1.89 (6) C5′ 4263 (2) 1074 (1) 2076 (5) 2.01 (6) C6′ 4465 (2) 1714 (1) 862 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.6 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) H2C2 707 (2) 367 (2) 332 (6) 4.2 (0.8) HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C8 737 (2) 184 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 737 (2) 184 (2) 184 (2) 184 (2) 410 (2) 413 (6) 2.9 (0.7) H1C8 737 (2) 184 (2) 194 (2) 410 (2) 413 (6) 2.9 (0.7) H1C6 552 (2) 165 (1) 726 (5) 1.5 (0.6) H2C6 636 (2) 181 (1) 800 (5) 2.2 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 737 (2) 58 (2) 45 (6) 40 (0.9) H1C9 733 (2) 184 (2) 652 (7) 4.6 (0.9) H1C9 733 (2) 184 (2) 652 (7) 4.6 (0.9) H1C9 733 (2) 184 (2) 652 (7) 4.6 (0.9) H1C9 733 (2) 184 (2) 652 (7) 4.6 (0.9) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.7) H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 991 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C15 625 (2) 331 (2) 408 (8) 6.6 (1.2) H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 337 (2) 174 (6) 3.7 (0.8) H3C13 591 (2) -12 (2) 991 (7) 4.0 (0.8) H3C13 591 (2) -12 (2) 991 (7) 4.0 (0.8) H3C13 591 (2) -12 (2) 991 (7) 4.0 (0.8) H3C13 591 (2) -12 (2) 991 (7) 4.0 (0.8) H3C13 591 (2) -12 (2) 991 (7) 4.0 (0.8) H3C13 591 (2) -12 (2) 991 (7) 4.0 (0.8) H3C13 591 (2) -12 (2) 991 (7) 4.0 (0.8) H3C13 591 (2) -12 (2) 991 (7) 4.0 (0.8) H3C13 591 (2) -12 (2) 991 (7) 4.0 (0.8) H3C13 591 (2) -12 (2) 991 (7) 4.0 (0.8) H3C15 588 (2) 277 (2) 990 (7) 4.5 (0.9) H3C15 588 (2) 277 (2) |       | , ,      |          | ` '      |             |
| C11 5922 (i) 400 (i) 6843 (5) 2.15 (6) C12 6100 (2) -275 (1) 5720 (7) 3.26 (8) C13 6127 (2) 349 (2) 9167 (6) 3.10 (7) C14 8099 (2) 2514 (2) 2730 (6) 2.60 (7) C15 5718 (2) 3167 (2) 8077 (5) 2.56 (7) O1′ 4701 (1) 1096 (1) 3999 (3) 2.17 (4) O2′ 3731 (1) -242 (1) 7005 (4) 2.53 (4) O3′ 2514 (1) 312 (1) 4681 (3) 2.46 (4) O4′ 2951 (1) 1024 (1) 782 (4) 3.07 (5) O6′ 4203 (1) 2321 (1) 1902 (4) 2.90 (5) C1′ 4640 (2) 464 (1) 5121 (5) 1.92 (6) C2′ 3811 (2) 384 (1) 5864 (5) 1.84 (6) C3′ 3291 (1) 362 (1) 3931 (5) 1.92 (6) C4′ 3410 (2) 1014 (1) 2646 (5) 1.89 (6) C5′ 4265 (2) 1074 (1) 862 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.6 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) H2C2 707 (2) 367 (2) 332 (6) 4.2 (0.8) HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C8 727 (2) 58 (2) 165 (1) 726 (5) 1.5 (0.6) H2C7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H1C9 773 (2) 184 (2) 652 (7) 184 (2) 652 (7) 194 (2) 652 (7) 194 (2) 652 (7) 194 (2) 652 (7) 194 (2) 653 (2) 165 (1) 726 (5) 1.5 (0.6) H2C7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C9 821 (2) 138 (2) 473 (6) 3.5 (0.7) H2C9 821 (2) 138 (2) 473 (6) 3.5 (0.8) H1C1 670 (2) 20 (2) 58 (2) 415 (6) 3.5 (0.7) H2C2 777 (2) 366 (2) 415 (6) 3.5 (0.7) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C15 580 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.0 (0.8) H2C14 836 (2) 277 (2) 991 (7) 4.0 (0.8) H2C15 580 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 588 (2) 473 (6) 3.7 (0.8) H3C15 588 (2) 473 (6) 3.7 (0.8) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2)  |       | , ,      |          |          |             |
| C12 6100 (2) -275 (1) 5720 (7) 3.26 (8) C13 6127 (2) 349 (2) 9167 (6) 3.10 (7) C14 8099 (2) 2514 (2) 2730 (6) 2.60 (7) C15 5718 (2) 3167 (2) 8077 (5) 2.56 (7) O1' 4701 (1) 1096 (1) 3999 (3) 2.17 (4) O2' 3731 (1) -242 (1) 7005 (4) 2.53 (4) O4' 2951 (1) 1024 (1) 782 (4) 3.07 (5) O6' 4203 (1) 2321 (1) 1902 (4) 2.90 (5) C1' 4640 (2) 464 (1) 5121 (5) 1.92 (6) C2' 3811 (2) 384 (1) 5864 (5) 1.84 (6) C3' 3291 (1) 362 (1) 3931 (5) 1.92 (6) C4' 3410 (2) 1014 (1) 2646 (5) 1.89 (6) C3' 3291 (1) 279 (2) 606 (5) 2.01 (6) C6' 4465 (2) 1714 (1) 862 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.6 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) H2C2 707 (2) 367 (2) 332 (6) 3.00 (0.7) H1C8 727 (2) 58 (2) 165 (1) 726 (5) 1.5 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C8 738 (2) 182 (2) 184 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C9 821 (2) 138 (2) 415 (6) 3.5 (0.7) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.0 (0.7) H2C13 600 (2) 77 (2) 367 (2) 363 (6) 3.0 (0.7) H2C8 738 (2) 415 (6) 3.5 (0.7) H2C8 738 (2) 415 (6) 3.5 (0.7) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.7) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.0 (0.8) H3C15 588 (2) 277 (2) 991 (7) 4.0 (0.8) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 588 (2) 277 (2) 991 (7)  |       |          |          | , ,      |             |
| C13 6127 (2) 349 (2) 9167 (6) 3.10 (7) C14 8099 (2) 2514 (2) 2730 (6) 2.60 (7) O1′ 4701 (1) 1096 (1) 3999 (3) 2.17 (4) O2′ 3731 (1) -242 (1) 7005 (4) 2.53 (4) O3′ 2514 (1) 312 (1) 4681 (3) 2.46 (4) O4′ 2951 (1) 1024 (1) 782 (4) 3.07 (5) C1′ 4640 (2) 464 (1) 5121 (5) 1.92 (6) C2′ 3811 (2) 384 (1) 5864 (5) 1.84 (6) C3′ 3291 (1) 362 (1) 3931 (5) 1.92 (6) C4′ 3410 (2) 1014 (1) 2076 (5) 2.01 (6) C5′ 4265 (2) 1074 (1) 2076 (5) 2.01 (6) C6′ 4466 (2) 1714 (1) 862 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.6 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) H2C2 707 (2) 367 (2) 332 (6) 4.2 (0.8) HC5′ 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C8 732 (2) 104 (2) 413 (6) 2.9 (0.7) H1C9 733 (2) 184 (2) 413 (6) 2.9 (0.7) H1C9 733 (2) 166 (1) 726 (5) 1.5 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C9 733 (2) 166 (1) 726 (5) 1.5 (0.6) H2C6 636 (2) 181 (1) 800 (5) 2.2 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C9 733 (2) 184 (2) 413 (6) 2.9 (0.7) H1C9 733 (2) 184 (2) 413 (6) 2.9 (0.7) H1C9 733 (2) 184 (2) 413 (6) 2.9 (0.7) H1C9 733 (2) 184 (2) 652 (7) 4.6 (0.9) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H2C13 670 (2) 363 (6) 3.0 (0.7) H2C2 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C12 660 (3) -31 (2) 408 (8) 6.6 (1.2) H1C13 670 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 670 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 540 (2) 363 (2) 337 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H2C15 540 (2) 363 (2) 337 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H2C15 540 (2) 363 (2) 337 (7) 4.9 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H2C15 540 (2) 363 (2) 337 (7) 4.6 (0.9) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H2C15 540 (2) 363 (2) 337 (7) 4.6 (0.9) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H2C15 540 (2) 363 (2) 337 (7) 4.6 (0.9) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H2C15 540 (2) 363 (2) 337 (7) 4.6 (0.9) H2C14 836 (2) 277 (2) 901 (7) 4.7 (0.9) H2C14 481 (2) 4(2) 403 (5) 2. |       |          |          |          |             |
| C14 8099 (2) 2514 (2) 2730 (6) 2.60 (7) C15 5718 (2) 3167 (2) 8077 (5) 2.56 (7) O1' 4701 (1) 1096 (1) 3999 (3) 2.17 (4) O2' 3731 (1) -242 (1) 7005 (4) 2.53 (4) O3' 2514 (1) 312 (1) 4681 (3) 2.46 (4) O4' 2951 (1) 1024 (1) 782 (4) 3.07 (5) O6' 4203 (1) 2321 (1) 1902 (4) 2.90 (5) C1' 4640 (2) 464 (1) 5121 (5) 1.92 (6) C2' 3811 (2) 384 (1) 5864 (5) 1.84 (6) C3' 3291 (1) 362 (1) 3931 (5) 1.92 (6) C4' 3410 (2) 1014 (1) 2646 (5) 1.89 (6) C5' 4265 (2) 1074 (1) 2076 (5) 2.01 (6) C6' 4465 (2) 1714 (1) 862 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.6 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) H2C2 707 (2) 367 (2) 363 (6) 3.0 (0.7) H1C6 552 (2) 165 (1) 726 (5) 1.5 (0.6) H2C6 636 (2) 181 (1) 800 (5) 2.2 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C8 738 (2) 65 (2) 664 (6) 4.0 (0.9) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H1C1 667 (2) -42 (2) 580 (6) 3.0 (0.7) H3C12 667 (2) -42 (2) 580 (6) 3.7 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.7 (0.8) H1C13 670 (2) 22 (2) 991 (7) 4.5 (0.9) H3C13 691 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 691 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 691 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 691 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 691 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 691 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 691 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 691 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 691 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 691 (2) 79 (2) 992 (7) 4.5 (0.9) H3C15 558 (2) 277 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 300 (6) 2.5 (0.7) H1C1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) H3C16 505 (2) 331 (2) 843 (6) 3.0 (0.7) 4.7 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0. |       |          | , ,      |          |             |
| C15  |       |          |          | , ,      |             |
| O1'         4701 (1)         1096 (1)         3999 (3)         2.17 (4)           O2'         3731 (1)         -242 (1)         7005 (4)         2.53 (4)           O3'         2514 (1)         312 (1)         4681 (3)         2.46 (4)           O4'         2951 (1)         1024 (1)         782 (4)         3.07 (5)           O6'         4203 (1)         2321 (1)         1902 (4)         2.90 (5)           C1'         4640 (2)         464 (1)         5121 (5)         1.92 (6)           C2'         3811 (2)         384 (1)         5864 (5)         1.84 (6)           C3'         3291 (1)         362 (1)         3931 (5)         1.92 (6)           C4'         3410 (2)         1014 (1)         2646 (5)         1.89 (6)           C5'         4265 (2)         1074 (1)         2076 (5)         2.01 (6)           C6'         4465 (2)         1714 (1)         862 (5)         2.46 (6)           HC1         711 (2)         279 (2)         606 (5)         2.6 (0.7)           H1C2         653 (2)         307 (2)         176 (7)         4.7 (0.9)           H2C2         707 (2)         367 (2)         332 (6)         4.2 (0.8)           HC5  |       |          |          | ` ,      |             |
| O2'         3731 (1)         -242 (1)         7005 (4)         2.53 (4)           O3'         2514 (1)         312 (1)         4681 (3)         2.46 (4)           O4'         2951 (1)         1024 (1)         782 (4)         3.07 (5)           O6'         4203 (1)         2321 (1)         1902 (4)         2.90 (5)           C1'         4640 (2)         464 (1)         5121 (5)         1.92 (6)           C2'         3811 (2)         384 (1)         5864 (5)         1.84 (6)           C3'         3291 (1)         362 (1)         3931 (5)         1.92 (6)           C4'         3410 (2)         1014 (1)         2646 (5)         1.89 (6)           C5'         4265 (2)         1074 (1)         2076 (5)         2.01 (6)           C6'         4465 (2)         1714 (1)         862 (5)         2.46 (6)           HC1         711 (2)         279 (2)         606 (5)         2.6 (0.7)           H1C2         653 (2)         307 (2)         176 (7)         4.7 (0.9)           H2C2         707 (2)         367 (2)         332 (6)         4.2 (0.8)           HC5         584 (2)         209 (2)         363 (6)         3.0 (0.7)           H1C6         <   |       |          |          | ` '      |             |
| O3' 2514 (1) 312 (1) 4681 (3) 2.46 (4) O4' 2951 (1) 1024 (1) 782 (4) 3.07 (5) O6' 4203 (1) 2321 (1) 1902 (4) 2.90 (5) C1' 4640 (2) 464 (1) 5121 (5) 1.92 (6) C2' 3811 (2) 384 (1) 5864 (5) 1.84 (6) C3' 3291 (1) 362 (1) 3931 (5) 1.92 (6) C4' 3410 (2) 1014 (1) 2646 (5) 1.89 (6) C5' 4265 (2) 1074 (1) 2076 (5) 2.01 (6) C6' 4465 (2) 1714 (1) 862 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.66 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) H2C2 707 (2) 367 (2) 332 (6) 4.2 (0.8) HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C6 552 (2) 165 (1) 726 (5) 1.5 (0.6) H2C6 636 (2) 181 (1) 800 (5) 2.2 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H2C9 821 (2) 138 (2) 473 (6) 3.5 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (3) -31 (2) 408 (8) 6.6 (1.2) H2C13 600 (3) -31 (2) 408 (8) 6.6 (1.2) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C15 558 (2) 277 (2) 58 (2) 417 (6) 3.7 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C15 558 (2) 277 (2) 58 (2) 491 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C15 558 (2) 277 (2) 58 (2) 491 (7) 5.3 (1.0) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H2C16 505 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H2C16 505 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H2C16 542 (2) 365 (2) 331 (2) 843 (6) 4.3 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H2C16 542 (2) 165 (2) 77 (1) 303 (5) 2.0 (0.6) HC4' 324 (2) 142 (2) 365 (2) 433 (9) 7.7 (1.3) H010 752 (3) 154 (2) 91 |       |          |          |          |             |
| O4'         2951 (1)         1024 (1)         782 (4)         3.07 (5)           O6'         4203 (1)         2321 (1)         1902 (4)         2.90 (5)           C1'         4640 (2)         464 (1)         5121 (5)         1.92 (6)           C2'         3811 (2)         384 (1)         5864 (5)         1.84 (6)           C3'         3291 (1)         362 (1)         3931 (5)         1.92 (6)           C4'         3410 (2)         1014 (1)         2646 (5)         1.89 (6)           C5'         4265 (2)         1074 (1)         2076 (5)         2.01 (6)           C6'         4465 (2)         1714 (1)         862 (5)         2.46 (6)           HC1         711 (2)         279 (2)         606 (5)         2.6 (0.7)           HC2 653 (2)         307 (2)         176 (7)         4.7 (0.9)           H2C2 707 (2)         367 (2)         332 (6)         4.2 (0.8)           HC5         584 (2)         209 (2)         363 (6)         3.0 (0.7)           H1C6         552 (2)         165 (1)         726 (5)         1.5 (0.6)           H2C6         636 (2)         181 (1)         800 (5)         2.2 (0.6)           H2C7         610 (2)         104 (2)<  |       |          | , ,      |          |             |
| O6'         4203 (1)         2321 (1)         1902 (4)         2.90 (5)           C1'         4640 (2)         464 (1)         5121 (5)         1.92 (6)           C2'         3811 (2)         384 (1)         5864 (5)         1.84 (6)           C3'         3291 (1)         362 (1)         3931 (5)         1.92 (6)           C4'         3410 (2)         1014 (1)         2646 (5)         1.89 (6)           C5'         4265 (2)         1074 (1)         2076 (5)         2.01 (6)           C6'         4465 (2)         1714 (1)         862 (5)         2.46 (6)           HC1         711 (2)         279 (2)         606 (5)         2.6 (0.7)           H1C2         653 (2)         307 (2)         176 (7)         4.7 (0.9)           H2C2         707 (2)         367 (2)         332 (6)         4.2 (0.8)           HC5         584 (2)         209 (2)         363 (6)         3.0 (0.7)           H1C6         552 (2)         165 (1)         726 (5)         1.5 (0.6)           H2C6         636 (2)         181 (1)         800 (5)         2.2 (0.6)           HC7         610 (2)         104 (2)         413 (6)         2.9 (0.7)           H2C8 <td< td=""><td>O4′</td><td></td><td></td><td></td><td></td></td<>   | O4′   |          |          |          |             |
| C1' 4640 (2) 464 (1) 5121 (5) 1.92 (6) C2' 3811 (2) 384 (1) 5864 (5) 1.84 (6) C3' 3291 (1) 362 (1) 3931 (5) 1.92 (6) C4' 3410 (2) 1014 (1) 2646 (5) 1.89 (6) C5' 4265 (2) 1074 (1) 2076 (5) 2.01 (6) C6' 4465 (2) 1714 (1) 862 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.6 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) H2C2 707 (2) 367 (2) 332 (6) 4.2 (0.8) HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C6 552 (2) 165 (1) 726 (5) 1.5 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C8 738 (2) 65 (2) 664 (6) 4.0 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H2C12 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C12 600 (3) -31 (2) 408 (8) 6.6 (1.2) H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H1C15 625 (2) 331 (2) 443 (6) 3.0 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 271 (2) 331 (2) 443 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) H2C15 540 (2) 365 (2) 331 (2) 443 (6) 3.0 (0.7) H2C15 540 (2) 365 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6) HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6) H1C6' 505 (2) 176 (2) 83 (6) 4.3 (0.9) 7.7 (1.3) H010 752 (3) 154 (2) 91 (8) 7.2 (1.2)      | O6′   | 4203 (1) | 2321 (1) | 1902 (4) |             |
| C3' 3291 (1) 362 (1) 3931 (5) 1.92 (6) C4' 3410 (2) 1014 (1) 2646 (5) 1.89 (6) C5' 4265 (2) 1074 (1) 2076 (5) 2.01 (6) C6' 4465 (2) 1714 (1) 862 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.6 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) H2C2 707 (2) 367 (2) 332 (6) 4.2 (0.8) HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C6 552 (2) 165 (1) 726 (5) 1.5 (0.6) H2C6 636 (2) 181 (1) 800 (5) 2.2 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C8 738 (2) 65 (2) 664 (6) 4.0 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H2C12 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H3C15 558 (2) 277 (2) 901 (7) 4.0 (0.8) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H3C16 552 (2) 331 (2) 433 (3) (3) (3) (3) (3) (3) (3) (3) (3) (   | C1′   | 4640 (2) |          | 5121 (5) |             |
| C4'         3410 (2)         1014 (1)         2646 (5)         1.89 (6)           C5'         4265 (2)         1074 (1)         2076 (5)         2.01 (6)           C6'         4465 (2)         1714 (1)         862 (5)         2.46 (6)           HC1         711 (2)         279 (2)         606 (5)         2.6 (0.7)           H1C2         653 (2)         307 (2)         176 (7)         4.7 (0.9)           H2C2         707 (2)         367 (2)         332 (6)         4.2 (0.8)           HC5         584 (2)         209 (2)         363 (6)         3.0 (0.7)           H1C6         552 (2)         165 (1)         726 (5)         1.5 (0.6)           H2C6         636 (2)         181 (1)         800 (5)         2.2 (0.6)           HC7         610 (2)         104 (2)         413 (6)         2.9 (0.7)           H1C8         727 (2)         58 (2)         415 (6)         3.5 (0.7)           H2C8         738 (2)         65 (2)         664 (6)         4.0 (0.9)           H1C9         773 (2)         184 (2)         652 (7)         4.6 (0.9)           H2C9         821 (2)         138 (2)         473 (6)         3.7 (0.8)           H2C12         6   | C2′   | 3811 (2) | 384 (1)  | 5864 (5) |             |
| C5' 4265 (2) 1074 (1) 2076 (5) 2.01 (6) C6' 4465 (2) 1714 (1) 862 (5) 2.46 (6) HC1 711 (2) 279 (2) 606 (5) 2.6 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) H2C2 707 (2) 367 (2) 332 (6) 4.2 (0.8) HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C6 552 (2) 165 (1) 726 (5) 1.5 (0.6) H2C6 636 (2) 181 (1) 800 (5) 2.2 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C8 738 (2) 65 (2) 664 (6) 4.0 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H2C12 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C12 660 (3) -31 (2) 408 (8) 6.6 (1.2) H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.0 (0.8) H1C16 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C17 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6) HC5' 442 (2) 165 (2) -57 (7) 3.9 (0.8) HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)   |       | 3291 (1) | 362 (1)  |          |             |
| C6'         4465 (2)         1714 (1)         862 (5)         2.46 (6)           HC1         711 (2)         279 (2)         606 (5)         2.6 (0.7)           H1C2         653 (2)         307 (2)         176 (7)         4.7 (0.9)           H2C2         707 (2)         367 (2)         332 (6)         4.2 (0.8)           HC5         584 (2)         209 (2)         363 (6)         3.0 (0.7)           H1C6         552 (2)         165 (1)         726 (5)         1.5 (0.6)           H2C6         636 (2)         181 (1)         800 (5)         2.2 (0.6)           HC7         610 (2)         104 (2)         413 (6)         2.9 (0.7)           H1C8         727 (2)         58 (2)         415 (6)         3.5 (0.7)           H2C8         738 (2)         65 (2)         664 (6)         4.0 (0.9)           H1C9         773 (2)         184 (2)         652 (7)         4.6 (0.9)           H2C9         821 (2)         138 (2)         473 (6)         3.7 (0.8)           H2C12         667 (2)         -42 (2)         580 (6)         3.5 (0.8)           H2C12         577 (2)         -69 (2)         639 (6)         2.9 (0.7)           H3C13         6   |       |          | 1014 (1) |          |             |
| HC1 711 (2) 279 (2) 606 (5) 2.6 (0.7) H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) H2C2 707 (2) 367 (2) 332 (6) 4.2 (0.8) HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C6 552 (2) 165 (1) 726 (5) 1.5 (0.6) H2C6 636 (2) 181 (1) 800 (5) 2.2 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C8 738 (2) 65 (2) 664 (6) 4.0 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H2C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H2C12 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C12 600 (3) -31 (2) 408 (8) 6.6 (1.2) H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 400 (3) (3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 558 (2) 277 (2) 991 (7) 4.7 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6) HC6' 505 (2) 176 (2) 83 (6) 4.3 (0.9) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) H0C4' 462 (3) 265 (2) 433 (9) 7.7 (1.3) H010 752 (3) 154 (2) 91 (8) 7.2 (1.2)   |       |          |          |          |             |
| H1C2 653 (2) 307 (2) 176 (7) 4.7 (0.9) H2C2 707 (2) 367 (2) 332 (6) 4.2 (0.8) HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C6 552 (2) 165 (1) 726 (5) 1.5 (0.6) H2C6 636 (2) 181 (1) 800 (5) 2.2 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C8 738 (2) 65 (2) 664 (6) 4.0 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H2C12 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC5' 442 (2) 142 (2) 358 (5) 2.2 (0.6) HC6' 324 (2) 165 (2) -57 (7) 3.9 (0.8) HC6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HC6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HC6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HC6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HC6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HC6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HC6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HC6' 422 (2) 165 (2) -57 (7) 3.9 (0.8)   |       |          | , ,      | ` '      | , ,         |
| H2C2 707 (2) 367 (2) 332 (6) 4.2 (0.8) HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C6 552 (2) 165 (1) 726 (5) 1.5 (0.6) H2C6 636 (2) 181 (1) 800 (5) 2.2 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C8 738 (2) 65 (2) 664 (6) 4.0 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H2C12 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6) HC5' 442 (2) 165 (2) -57 (7) 3.9 (0.8) H2C6' 422 (2) 165 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)  |       |          |          |          |             |
| HC5 584 (2) 209 (2) 363 (6) 3.0 (0.7) H1C6 552 (2) 165 (1) 726 (5) 1.5 (0.6) H2C6 636 (2) 181 (1) 800 (5) 2.2 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C8 738 (2) 65 (2) 664 (6) 4.0 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H2C12 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C12 600 (3) -31 (2) 408 (8) 6.6 (1.2) H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.9 (0.7) HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6) HC6' 324 (2) 165 (2) -57 (7) 3.9 (0.8) HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)  |       |          |          | ` '      | . ,         |
| H1C6   |       | . ,      | . 1./    | ` '      |             |
| H2C6 636 (2) 181 (1) 800 (5) 2.2 (0.6) HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C8 738 (2) 65 (2) 664 (6) 4.0 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H2C12 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C12 600 (3) -31 (2) 408 (8) 6.6 (1.2) H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H3C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC3' 343 (2) 176 (2) 124 (5) 2.4 (0.6) HC5' 442 (2) 165 (2) 176 (2) 83 (6) 4.3 (0.9) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) H0C4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)  |       |          |          | ` '      |             |
| HC7 610 (2) 104 (2) 413 (6) 2.9 (0.7) H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C8 738 (2) 65 (2) 664 (6) 4.0 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H2C12 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C12 600 (3) -31 (2) 408 (8) 6.6 (1.2) H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC3' 343 (2) 176 (2) 124 (5) 2.4 (0.6) HC5' 442 (2) 161 (2) 124 (5) 2.4 (0.6) HC6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)  |       |          |          | ` '      |             |
| H1C8 727 (2) 58 (2) 415 (6) 3.5 (0.7) H2C8 738 (2) 65 (2) 664 (6) 4.0 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H2C12 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C12 600 (3) -31 (2) 408 (8) 6.6 (1.2) H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6) HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6) HC6' 505 (2) 176 (2) 83 (6) 4.3 (0.9) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)  |       | . ,      | . ,      |          |             |
| H2C8 738 (2) 65 (2) 664 (6) 4.0 (0.9) H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H2C12 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C12 600 (3) -31 (2) 408 (8) 6.6 (1.2) H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6) HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6) HC6' 505 (2) 176 (2) 83 (6) 4.3 (0.9) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)  |       |          | , ,      | ` '      | , ,         |
| H1C9 773 (2) 184 (2) 652 (7) 4.6 (0.9) H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H2C12 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C12 600 (3) -31 (2) 408 (8) 6.6 (1.2) H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.9 (0.7) HC5' 442 (2) 142 (2) 358 (5) 2.2 (0.6) HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6) H1C6' 505 (2) 176 (2) 83 (6) 4.3 (0.9) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)   |       |          |          | ` '      | ` '         |
| H2C9 821 (2) 138 (2) 473 (6) 3.7 (0.8) H1C12 667 (2) -42 (2) 580 (6) 3.5 (0.8) H2C12 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C12 600 (3) -31 (2) 408 (8) 6.6 (1.2) H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC3' 324 (2) 142 (2) 358 (5) 2.2 (0.6) HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6) H1C6' 505 (2) 176 (2) 83 (6) 4.3 (0.9) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)  | H1C9  |          |          | * *      | ` '         |
| H2C12 577 (2) -69 (2) 639 (6) 2.9 (0.7) H3C12 600 (3) -31 (2) 408 (8) 6.6 (1.2) H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.9 (0.7) HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6) HC5' 442 (2) 165 (2) 75 (7) 3.9 (0.8) HC6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)   | H2C9  |          | 138 (2)  |          |             |
| H3C12 600 (3) -31 (2) 408 (8) 6.6 (1.2) H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6) HC5' 442 (2) 165 (2) 79 (1) 695 (5) 2.0 (0.6) HC5' 442 (2) 165 (2) 124 (5) 2.4 (0.6) H1C6' 505 (2) 176 (2) 83 (6) 4.3 (0.9) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)  | H1C12 |          |          | 580 (6)  | 3.5 (0.8)   |
| H1C13 670 (2) 22 (2) 941 (7) 5.3 (1.0) H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6) HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6) H1C6' 505 (2) 176 (2) 83 (6) 4.3 (0.9) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)   | H2C12 | 577 (2)  | -69(2)   | 639 (6)  | 2.9 (0.7)   |
| H2C13 600 (2) 79 (2) 992 (7) 4.5 (0.9) H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6) HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6) H1C6' 505 (2) 176 (2) 83 (6) 4.3 (0.9) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)  |       |          |          |          |             |
| H3C13 591 (2) -12 (2) 971 (7) 4.0 (0.8) H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8) H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6) HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6) H1C6' 505 (2) 176 (2) 83 (6) 4.3 (0.9) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)   |       |          |          | ` '      |             |
| H1C14 794 (2) 293 (2) 174 (6) 3.7 (0.8)  H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7)  H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7)  H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9)  H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9)  HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7)  HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6)  HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6)  HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6)  HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6)  H1C6' 505 (2) 176 (2) 83 (6) 4.3 (0.9)  H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8)  HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3)  HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)  |       | , ,      |          | • •      |             |
| H2C14 836 (2) 272 (2) 390 (6) 2.5 (0.7) H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6) HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6) H1C6' 505 (2) 176 (2) 83 (6) 4.3 (0.9) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)   |       |          |          |          | ` /         |
| H1C15 625 (2) 331 (2) 843 (6) 3.0 (0.7) H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6) HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6) H1C6' 505 (2) 176 (2) 83 (6) 4.3 (0.9) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)   |       |          |          |          |             |
| H2C15 540 (2) 363 (2) 837 (7) 4.6 (0.9) H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9) HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7) HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6) HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6) HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6) HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6) H1C6' 505 (2) 176 (2) 83 (6) 4.3 (0.9) H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8) HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3) HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)   |       |          |          | , ,      |             |
| H3C15 558 (2) 277 (2) 901 (7) 4.7 (0.9)<br>HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7)<br>HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6)<br>HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6)<br>HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6)<br>HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6)<br>H1C6' 505 (2) 176 (2) 83 (6) 4.3 (0.9)<br>H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8)<br>HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3)<br>HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)  |       |          |          |          |             |
| HC1' 481 (2) 4 (2) 403 (5) 2.9 (0.7)<br>HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6)<br>HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6)<br>HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6)<br>HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6)<br>H1C6' 505 (2) 176 (2) 83 (6) 4.3 (0.9)<br>H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8)<br>HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3)<br>HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)   |       |          |          | . ,      | ` ,         |
| HC2' 366 (2) 79 (1) 695 (5) 2.0 (0.6)<br>HC3' 343 (2) -7 (1) 303 (5) 2.0 (0.6)<br>HC4' 324 (2) 142 (2) 358 (5) 2.2 (0.6)<br>HC5' 442 (2) 61 (2) 124 (5) 2.4 (0.6)<br>H1C6' 505 (2) 176 (2) 83 (6) 4.3 (0.9)<br>H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8)<br>HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3)<br>HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)   |       |          |          |          |             |
| HC3'       343 (2)       -7 (1)       303 (5)       2.0 (0.6)         HC4'       324 (2)       142 (2)       358 (5)       2.2 (0.6)         HC5'       442 (2)       61 (2)       124 (5)       2.4 (0.6)         H1C6'       505 (2)       176 (2)       83 (6)       4.3 (0.9)         H2C6'       422 (2)       165 (2)       -57 (7)       3.9 (0.8)         HO4       462 (3)       265 (2)       433 (9)       7.7 (1.3)         HO10       752 (3)       154 (2)       91 (8)       7.2 (1.2)  |       |          |          |          |             |
| HC4'     324 (2)     142 (2)     358 (5)     2.2 (0.6)       HC5'     442 (2)     61 (2)     124 (5)     2.4 (0.6)       H1C6'     505 (2)     176 (2)     83 (6)     4.3 (0.9)       H2C6'     422 (2)     165 (2)     -57 (7)     3.9 (0.8)       HO4     462 (3)     265 (2)     433 (9)     7.7 (1.3)       HO10     752 (3)     154 (2)     91 (8)     7.2 (1.2)  |       |          |          | • /      |             |
| HC5'     442 (2)     61 (2)     124 (5)     2.4 (0.6)       H1C6'     505 (2)     176 (2)     83 (6)     4.3 (0.9)       H2C6'     422 (2)     165 (2)     -57 (7)     3.9 (0.8)       HO4     462 (3)     265 (2)     433 (9)     7.7 (1.3)       HO10     752 (3)     154 (2)     91 (8)     7.2 (1.2)   |       |          |          |          | , ,         |
| H1C6' 505 (2) 176 (2) 83 (6) 4.3 (0.9)<br>H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8)<br>HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3)<br>HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)  |       |          |          | ` '      | , ,         |
| H2C6' 422 (2) 165 (2) -57 (7) 3.9 (0.8)<br>HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3)<br>HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)  |       |          |          | 1 1      |             |
| HO4 462 (3) 265 (2) 433 (9) 7.7 (1.3)<br>HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)   |       |          |          | ` '      |             |
| HO10 752 (3) 154 (2) 91 (8) 7.2 (1.2)  |       |          |          |          | . ,         |
| HO14 887 (4) 228 (3) 55 (12) 13.0 (2.1)  |       |          |          | 91 (8)   |             |
|  | HO14  | 887 (4)  | 228 (3)  | 55 (12)  | 13.0 (2.1)  |

Coordinates ( $\times 10^3$ ).

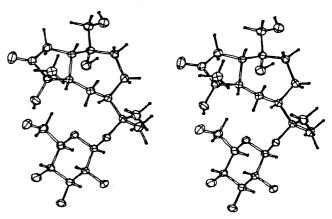
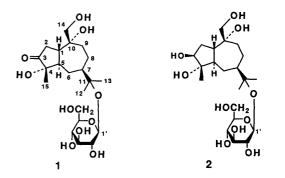


Fig. 1. ORTEP Drawing of 1



1.5418 Å) radiation and the  $2\theta-\omega$  scan technique. After correcting for Lorentz and polarization effects, 1816 independent reflections were observed,  $I \ge 2.3\sigma$  (I). The structure was solved by the direct method with the MULTAN 82<sup>2)</sup> series of programs. A block-diagonal least-squares refinement with anisotropic nonhydrogen atoms and isotropic hydrogen atoms lowered the R value to 0.036. The final atomic coordinates are listed in Table II and the ORTEP drawing is shown in Fig. 1. Consequently, the structure including the absolute configuration was concluded to be as shown in the formula.

Atractyloside B (2), a white powder,  $[\alpha]_D - 7.8^\circ$  showed a  $[M+Na]^+$  at m/z 473 in the positive FAB-MS. The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra (Table I) of 2 were similar to those of 1, except that a signal at  $\delta$  221.4 (s) due to the carbonyl group at C-3 in the <sup>13</sup>C-NMR spectrum of 1 had disappeared and a new signal at 79.7 (d) assignable to carbon bearing a sechydroxyl group appeared in that of 2. Reduction of 1 with NaBH<sub>4</sub> afforded a product identical with 2, and thus the structure of 2 was concluded to be 1,5-trans-3,4,10,11,14-pentahydroxyguaiane 11-O- $\beta$ -D-glucopyranoside. The configuration at C<sub>3</sub>-OH was concluded to be  $\beta$  from the observation of the nuclear Overhauser effects (NOE) between H<sub>3</sub>-15 and H<sub>2</sub>-6, H-1, H-2, and between H-3 and H-5, H-2 $\alpha$  in the <sup>1</sup>H-NMR spectrum of the aglycone (2a) obtained by enzymatic hydrolysis of 2.

Eudesmane-Type Glycosides Atractylosides C (3), a white powder,  $[\alpha]_D + 12.0^\circ$  (MeOH), D (4), a white powder,  $[\alpha]_D - 15.0^\circ$  (MeOH), E (5), a white powder,  $[\alpha]_D - 39.4^\circ$  (MeOH) and F (6), a white powder,  $[\alpha]_D - 99.8^\circ$  (MeOH) showed the respective cluster ion peaks due to the molecular at m/z 399  $[M-H]^-$ , 561  $[M-H]^-$ , 717  $[M+Na]^+$  and 825  $[M-H]^-$  in the positive or negative FAB-MS. On

November 1989 2997

Table III.  $^{13}$ C-NMR Data for 3, 3a, 4, 5, 6, 7, 7a, 8 and 9 (in Pyridine- $d_5$ )

|           | 3     | 3a    | 4                 | 5                   | 6                   | 7     | 7a    | 8              | 9                  |
|-----------|-------|-------|-------------------|---------------------|---------------------|-------|-------|----------------|--------------------|
| C-1       | 52.1  | 52.2  | 48.1              | 47.9                | 48.1                | 49.3  | 49.8  | 46.8           | 54.5               |
| C-2       | 67.3  | 67.3  | 75.3              | 75.6                | 75.8                | 73.4  | 73.5  | 84.4           | 194.8              |
| C-3       | 47.6  | 49.7  | 47.7              | 45.1                | 45.4                | 79.6  | 79.7  | 78.9           | 151.0(s)           |
| C-4       | 150.2 | 150.6 | 150.6             | 148.5               | 148.7               | 152.3 | 152.6 | 150.3          | 146.9 (s)          |
| C-5       | 49.8  | 50.0  | 49.7              | 49.4                | 49.6                | 48.6  | 48.5  | 48.6           | 48.5               |
| C-6       | 22.2  | 22.5  | 22.2              | 22.0                | 22.1                | 22.2  | 28.5  | 22.1           | 22.1               |
| C-7       | 48.8  | 49.7  | 48.7              | 48.5                | 48.7                | 48.5  | 49.4  | 48.0           | 47.5               |
| C-8       | 24.8  | 25.3  | 24.9              | 24.8                | 25.0                | 25.4  | 25.6  | 25.4           | 24.7               |
| C-9       | 41.4  | 41.5  | 41.3              | 41.0                | 41.2                | 41.1  | 41.2  | 40.7           | 40.0               |
| C-10      | 35.5  | 35.5  | 35.5              | 35.1                | 35.2                | 35.5  | 35.4  | 35.1           | 37.0               |
| C-11      | 79.5  | 71.4  | 79.4              | 79.3                | 79.5                | 79.5  | 71.4  | 80.4           | 79.5               |
| C-12      | 24.1  | 27.7  | 24.0              | 23.6                | 23.9                | 24.1  | 27.1  | 24.0           | 23.5               |
| C-13      | 25.2  | 28.1  | 24.8              | 24.5                | 24.9                | 24.8  | 27.7  | 24.8           | 25.4               |
| C-14      | 17.7  | 17.6  | 17.4              | 17.2                | 17.4                | 17.8  | 17.8  | 17.4           | 15.2               |
| C-15      | 107.4 | 107.4 | 108.1             | 108.1               | 108.3               | 104.8 | 104.8 | 106.3          | 16.9               |
| Glc-1'    | 98.7  |       | 98.7              | 98.4                | 98.7                | 98.7  |       | 98.7           | 98.7               |
| Glc-2'    | 75.4  |       | $75.3^{a}$        | 75.0 <sup>a</sup> ) | 75.3 <sup>a</sup> ) | 75.7  |       | 74.7           |                    |
| Glc-3'    | 79.0  |       | $78.7^{b}$        |                     |                     | 78.9  |       | $78.0^{b}$     | 78.9 <sup>b)</sup> |
| Glc-4'    | 72.0  |       | 71.7°             |                     | $71.9^{c}$          | 72.0  |       | $72.0^{\circ}$ |                    |
| Glc-5'    | 78.1  |       | $78.0^{d}$        |                     | 77.9                | 78.6  |       | 77.8           | $78.4^{d}$         |
| Glc-6'    | 63.2  |       | $62.8^{e}$        | 62.9                | 69.0                | 63.1  |       | 63.1           | $63.1^{e)}$        |
| Glc-1"    |       |       | 103.2             | 103.4               | 103.3               |       |       | 104.3          | 105.7              |
| Glc-2"    |       |       | $75.4^{a}$        | 75.2 <sup>a</sup> ) | 75.4 <sup>a</sup>   | )     |       | 75.2°          |                    |
| Glc-3''   |       |       | $79.0^{b}$        | 78.7 <sup>b)</sup>  | $79.0^{b)}$         | )     |       | $78.3^{b}$     | $78.6^{b}$         |
| Glc-4"    |       |       | $72.0^{c}$        | 71.8 <sup>c)</sup>  | $72.0^{c}$          | 1     |       | $71.8^{\circ}$ | 71.4 <sup>c)</sup> |
| Glc-5"    |       |       | $78.4^{d}$        | 77.0                | 77.9                |       |       | 77.0           | $78.1^{d}$         |
| Glc-6''   |       |       | 63.2 <sup>e</sup> | 69.2                | 69.2                |       |       | 69.1           | $62.7^{e}$         |
| Api-1'''  |       |       |                   | 110.9               | 111.2               |       |       | 111.2          |                    |
| Api-2"    |       |       |                   | 76.8                | $77.0^{d}$          | •     |       | 76.7           |                    |
| Api-3'''  |       |       |                   | 80.3                | 80.5                |       |       | 79.4           |                    |
| Api-4'''  |       |       |                   | 74.8                | 75.1                |       |       | 75.2           |                    |
| Api-5'''  |       |       |                   | 65.5                | 65.8                |       |       | 65.8           |                    |
| Api-1""   |       |       |                   |                     | 111.2               |       |       |                |                    |
| Api-2""   |       |       |                   |                     | $76.2^{d}$          | 1     |       |                |                    |
| Api-3'''' |       |       |                   |                     | 80.5                |       |       |                |                    |
| Api-4'''' |       |       |                   |                     | 75.1                |       |       |                |                    |
| Api-5'''' |       |       |                   |                     | 65.8                |       |       |                |                    |

a-e) may be interchangeable in each column.

enzymatic hydrolysis, they all gave the same aglycone (3a), a white powder,  $[\alpha]_D + 31.7^{\circ}$  (MeOH) (from 3), whose <sup>1</sup>H-NMR spectrum was analogous to that of  $\beta$ -eudesmol, but it exhibited a signal (1H, dt, J=3, 12 Hz) due to a carbinol proton. Based on this coupling constant, it was concluded to be pterocarpol  $(2\alpha$ -hydroxy- $\beta$ -eudesmol).<sup>3)</sup> This was also confirmed by the <sup>1</sup>H-<sup>1</sup>H COSY and <sup>13</sup>C-NMR spectra (Table III). Liberated sugars were also detected by thin layer chromatography (TLC); glucose was obtained from 3 and 4, and glucose and apiose from 5 and 6. The sugar linkages were determined from the glycosylation shifts.<sup>1)</sup> As listed in Table III, shifts at C-11 (+8.1 ppm) in 3, and at C-2 (+8.0 - +8.5 ppm) and C-11 (+7.9-+8.1 ppm) in 4, 5 and 6 compared with those in 3a were observed in the <sup>13</sup>C-NMR spectra. Moreover, the <sup>13</sup>C-NMR data indicated the presence of the  $\beta$ -D-apiofuranosyl- $(1\rightarrow 6)$ - $\beta$ -D-glucopyranosyl moiety in 5 and 6. Therefore, the structures of 3 and 4 could be represented as  $11-O-\beta$ -Dglucopyranosyl pterocarpol and 2,11-di-O-β-D-glucopyranosyl pterocarpol. Atractyloside F (6) was formulated as 2,11-di-O- $\beta$ -D-apiofuranosyl- $(1 \rightarrow 6)$ - $\beta$ -D-glucopyranosyl pterocarpol. The electron impact mass spectrum (EI-MS) of the acetate of 5 showed peaks at m/z 766, 547, 331 and 259 due to [M-hexose-OH]<sup>+</sup>, pentosyl hexosyl cation,

hexosyl cation and pentosyl cation, rspectively, in the EI-MS. Since the terminal hexosyl moiety attached to the *tert*-hydroxyl group is readily cleaved, the occurrence of the prominent peak at m/z 547 suggested that the terminal glucose is linked to the C-11-OH. Thus, the structure of 5 was tentatively deduced to be 2-O- $\beta$ -D-apiofuranosyl- $(1 \rightarrow 6)$ - $\beta$ -D-glucopyranosyl pterocarpol 11-O- $\beta$ -D-glucopyranoside.

Atractyloside G (7), a white powder,  $[\alpha]_D + 2.2^\circ$  (MeOH) showed a cluster ion  $[M-H]^-$  at m/z 415 in the negative FAB-MS. Enzymatic hydrolysis provided an aglycone (7a) and glucose. The <sup>1</sup>H-NMR signals of 7a resembled those of pterocarpol (3a), except that a change in the signal pattern at H-2 (ddd, J=5, 9, 12 Hz,  $\delta$  4.11) and appearance of the oxygenated methine proton signal (1H, brd, J=9 Hz) at  $\delta$  4.35 were observed. The <sup>1</sup>H-<sup>1</sup>H COSY of 7a revealed a correlation of the above two protons, and thus 7a was regarded as  $3\beta$ -hydroxypterocarpol. The <sup>13</sup>C-NMR data (Table III) were also consistent with the above <sup>1</sup>H-NMR data. Furthermore, the <sup>13</sup>C-NMR data suggested the presence of a  $\beta$ -D-glucopyranosyl residue attached to the C-11-OH. Therefore, the structure of 7 was represented as 11-O- $\beta$ -D-glucopyranosyl  $3\beta$ -hydroxypterocarpol.

Atractyloside H (8), a white powder,  $[\alpha]_D - 33.2^\circ$  (MeOH) exhibited a  $[M+Na]^+$  at m/z 733, giving an aglycone identical with  $3\beta$ -hydroxypterocarpol (7a) together with glucose and apiose. Analysis of the  $^{13}$ C-NMR spectrum of 8 disclosed the presence of apiofuranosyl- $(1\rightarrow6)$ - $\beta$ -D-glucopyranosyl and  $\beta$ -D-glucopyranosyl residues in the molecule. The appearance of a prominent peak at m/z 553 due to a  $[M-glc-H_2O+Na]^+$  in the positive FAB-MS suggested that the glucosyl residue was linked to

2998 Vol. 37, No. 11

the C-11-OH as in 5. Therefore, the structure of 8 was tentatively expressed as shown in the formula.

Atractyloside I (9), colorless needles, mp 156-158 °C,  $[\alpha]_D + 19.7^\circ$ , showed cluster ion peaks due to  $[M+H]^+$  and  $[M + Na]^+$  at m/z 577 and 599, respectively, in the positive FAB-MS. The <sup>1</sup>H-NMR spectrum of 9 exhibited singlet signals due to methyl groups at  $\delta$  0.92, 1.24, 1.29 and 2.01, and signals of two anomeric protons of  $\beta$ -Dglucopyranosyl residues. The 13C-NMR spectrum displayed signals ascribable to two glucopyranosyl residues and fifteen carbons, among which the signals at  $\delta$  194.8 (s), 154.3 (s) and 147.1 (s) suggested the presence of an  $\alpha, \beta$ unsaturated carbonyl group. Since signals due to the olefinic protons in this group were shifted toward lower field than usual, the presence of a hydroxyl group at the  $\alpha$ position on the  $\alpha,\beta$ -unsaturated residue was suggested. Moreover, the molecular weight in the MS also supported the above evidence. The circular dichroism (CD) spectrum of 9 showed a positive Cotton effect having a maximum at 258 nm and a negative Cotton effect having a maximum at 323 nm.<sup>4)</sup> The <sup>1</sup>H-NMR spectrum of the aglycone (9a) obtained by enzymatic hydrolysis of 9 displayed a vinyl methyl signal at  $\delta$  2.00 (d, J=2 Hz) ascribable to H<sub>3</sub>-15. From the above accumulated evidence, the structure of 9 was determined as 2-keto-3-hydroxy-β-eudesmol 3,11-di-O- $\beta$ -D-glucopyranoside.

## Experimental

Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-360 digital polarimeter. The ultraviolet (UV) and CD spectra were obtained with a Hitachi 556 type spectrometer and a JASCO J-500 spectrometer, respectively. The infrared (IR) spectra were recorded on a Hitachi 260-10 spectrometer. The EI-MS and FAB-MS were taken with JEOL JMS-01SG and JEOL JMS-DX-300 instruments, respectively. The <sup>1</sup>H- (400 MHz) and <sup>13</sup>C- (100.4 MHz) NMR spectra were recorded on a JEOL JNM-GX-400 spectrometer with tetramethylsilane as an internal standard, and chemical shifts are given in  $\delta$  (ppm). X-Ray intensities were collected with an Enraf-Nonius CAD4F-11 automatic diffractometer at room temperature. Column chromatography was performed with Kieselgel 60 (70—230 mesh, Merck), Sephadex LH-20 (25—100  $\mu$ , Pharmacia Fine Chemical Co., Ltd.) and MCI gel CHP 20P (75-150 μ, Mitsubishi Chemical Industries, Ltd.) and Bondapak C<sub>18</sub> (Waters Associates). TLC was conducted on precoated Kieselgel 60 F<sub>254</sub> plates (Merck, 0.2 mm thick).

Isolation of Atractylosides The fresh rhizomes (3.2 kg) of *A. lancea* DC. were extracted twice with 70% acetone. Concentration of the extracts under reduced pressure afforded a residue (170 g), which was partitioned between benzene and water. The aqueous layer (150 g) was chromatographed on an MCI gel CHP 20P column. Elution with water containing increasing amounts of methanol yielded nine fractions; fr. 1 (0.3 g), fr. 2 (3.3 g), fr. 3 (1.9 g), fr. 4 (1.1 g), fr. 5 (0.8 g), fr. 6 (0.7 g), fr. 7 (2.0 g), fr. 8 (1.0 g) and fr. 9 (1.6 g). Each fraction was further purified as shown in Chart 1 to give atractylosides A—I (1—9) together with the two known compounds, L-tryptophan, colorless plates, mp 237—239 °C,  $[\alpha]_D^{28} - 49.8^\circ$  (c = 0.25, pyridine), and syringin, colorless crystals, mp  $184 - 186^\circ$ C,  $[\alpha]_D^{27} - 23.9^\circ$  (c = 0.50, MeOH). <sup>1</sup>H-NMR (methanol- $d_4$ )  $\delta$ : 3.22—3.78 (glc H<sub>2</sub>-6), 3.85 (6H, s, OMe×2), 4.22 (2H, dd, J = 2, 6Hz, H<sub>2</sub>-9), 4.88 (1H, d, J = 7 Hz, glc H-1), 6.33 (1H, dt, J = 6, 16 Hz, H-8), 6.55 (1H, d, J = 16 Hz, H-7), 6.74 (2H, s, H-2,6).

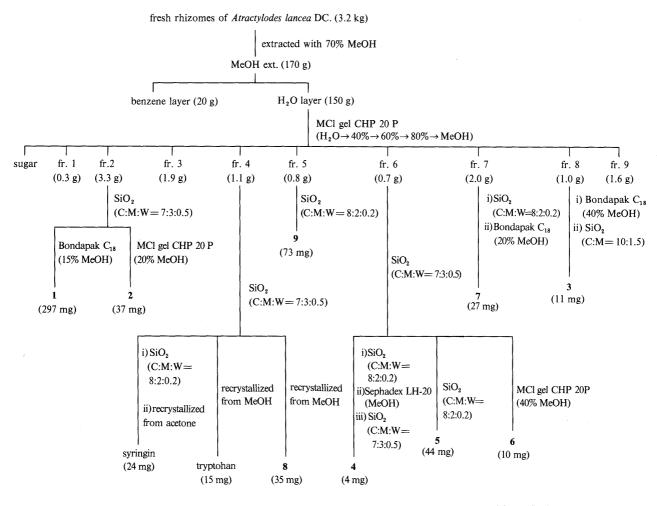
Atractyloside A (1) Colorless needles, mp 227—230 °C,  $[\alpha]_D^{27} + 20.0^\circ$  (c = 0.52, 50% MeOH). CD ( $c = 3.35 \times 10^{-4}$ , MeOH) [ $\theta$ ] (nm):  $+ 5.77 \times 10^3$  (304), 0 (324),  $-0.209 \times 10^3$  (350). Positive FAB-MS m/z: 541 [M+H+glycerol]<sup>+</sup>, 449 [M+H]<sup>+</sup>, 431 [M+H-H<sub>2</sub>O]<sup>+</sup>, 253, 252, 235, 233. <sup>1</sup>H-NMR (pyridine- $d_5$ ) δ: 1.37, 1.40, 1.45 (each 3H, s, H<sub>3</sub>-12,13,15), 1.45 (1H, td, J = 11, 13 Hz, H-6), 1.74 (1H, td, J = 7, 14 Hz, H-8), 2.13 (1H, dd, J = 8, 13 Hz, H-9), 2.40 (1H, ddd, J = 9, 10, 11 Hz, H-1), 2.46 (1H, ddd, J = 9, 10, 11 Hz, H-2), 2.77 (1H, t, J = 11 Hz, H-5), 2.80 (1H, dd, J = 5, 13 Hz, H-6), 3.09 (1H, dd, J = 9, 19 Hz, H-2), 3.84 (1H, m, glc H-5), 3.86 (2H, br s, H<sub>2</sub>-14), 3.94 (1H, dd, J = 8, 9 Hz, glc H-2), 4.11 (1H, t, J = 9 Hz, glc H-4), 4.24 (1H, t, J = 9 Hz, glc H-3), 4.26 (1H, dd, J = 5, 10 Hz, glc H-6), 4.44 (1H, dd, J = 1, 10 Hz, glc H'-6), 4.97 (1H, d, J = 8 Hz, glc H-1).

Enzymatic Hydrolysis of 1 A solution of 1 (20 mg) and crude naringinase (20 mg) in water was incubated at 38 °C for 8 h. After purification of the product by silica gel column chromatography with chloroformmethanol = 7:1, 1 gave the aglycone (1a) (5.7 mg) and p-glucose,  $[\alpha]_D^{20} + 34.7^\circ$  (c=0.51, H<sub>2</sub>O). 1a: a colorless powder,  $[\alpha]_D^{23} + 23.5^\circ$  (c=0.57, MeOH). <sup>1</sup>H-NMR (pyridine- $d_5$ ) δ: 1.41, 1.42, 1.43 (each 3H, s, H<sub>3</sub>-12,13,15), 1.61 (1H, td, J=11, 12 Hz, H-6), 1.91 (1H, td, J=9, 12 Hz, H-8), 2.08 (1H, m, H-7), 2.17 (1H, dd, J=9, 14 Hz, H-9), 2.44 (1H, td, J=9, 14 Hz, H-1), 2.51 (1H, ddd, J=5, 9, 12 Hz, H'8), 2.60 (1H, dd, J=9, 14 Hz, H-9), 2.74 (1H, dd, J=9, 19 Hz, H-2), 2.77 (1H, m, H'-6), 2.82 (1H, dd, J=11, 12 Hz, H-5), 3.17 (1H, dd, J=9, 19 Hz, H'-2), 3.87 (2H, s, H<sub>2</sub>-14).

Oxidation of 1 with *m*-Chloroperbenzoic Acid *m*-Chloroperbenzoic acid (20 mg) was added to a solution of 1 (20 mg) in water (10 ml). The mixture was then stirred for 1 h at room temperature and evaporated under reduced pressure to give a residue, which was subjected to silica gel chromatography with CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O=7:3:0.5 to afford 1b (14 mg). 1b: a white powder,  $[\alpha]_{1}^{11}$  +59.1° (c=0.23, MeOH). Negative FAB-MS m/z: 537 [M+glycerol-H<sub>2</sub>O-H]<sup>-</sup>, 445 [M-H<sub>2</sub>O-H]<sup>-</sup>. <sup>1</sup>H-NMR (pyridine- $d_{5}$ )  $\delta$ : 1.24, 1.39 (each 3H, s, H<sub>3</sub>-12,13), 1.25—1.40 (2H, m, H-6,8), 1.93—2.05 (3H, m, H-7, H<sub>2</sub>-9), 2.28 (3H, s, H<sub>3</sub>-15), 2.35 (1H, dd, J=7, 14 Hz, H'-8), 2.42 (1H, dd, J=10, 12 Hz, H-1), 2.59 (1H, br d, J=12 Hz, H-5), 3.05 (1H, t, J=10 Hz, H-2), 3.18 (1H, dd, J=3, 12 Hz, H'-6), 3.23 (1H, t, J=10 Hz, H'-2), 3.90 (1H, m, glc H-5), 3.92 (1H, dd, J=8, 9 Hz, glc H-2), 3.99, 4.04 (each 1H, d, J=12 Hz, H<sub>2</sub>-14), 4.11 (1H, t, J=9 Hz, glc H-3), 4.26 (1H, dd, J=6, 12 Hz, glc H-6), 4.51 (1H, dd, J=3, 12 Hz, glc H'-6), 4.98 (1H, d, J=8 Hz, glc H-1).

X-Ray Analysis of 1 Crystal data are as follows:  $C_{21}H_{36}O_{10}$ ,  $M_r=448.51$ , orthorhombic, space group  $P2_12_12_1$ , a=17.433 (4), b=19.447 (4), c=6.347 (1) Å, V=2151.7 (7) ų, Z=4,  $D_c=1.384$  g·cm³, F(000)=968, T=298 K. Intensity data were recorded on an Enraf-Nonius CAD4F-11 four circle automatic diffractometer with graphite monochromated  $MoK_{\alpha}$  radiation. One thousand eight hundred and sixteen independent reflections were observed on the basis of the criterion  $F_0>2\sigma(F_0)$ . The structures were solved by the direct method using MULTAN 82 and refined by the block-diagonal least-squares method. The final refinements with anisotropic temperature factors lowered the R value to 0.036.

Atractyloside B (2) A white powder,  $[α]_0^{27} - 7.8^\circ$  (c = 1.00, MeOH). Positive FAB-MS m/z: 473 [M+Na]<sup>+</sup>. <sup>1</sup>H-NMR (pyridine- $d_5$ ) δ: 1.38, 1.45, 1.52 (each 3H, s, H<sub>3</sub>-12,13,15), 1.35—1.45 (2H, m, H-6,8), 1.95 (3H, m, H'-6, H-7,9), 2.18 (1H, m, H-1), 2.28 (1H, t-like, J = 11 Hz, H-2), 2.65 (1H, t, J = 11 Hz, H-5), 2.86 (3H, m, H'-2,8,9), 3.79, 3.86 (each 1H, d, J = 10 Hz, H<sub>2</sub>-14), 3.85 (1H, m, glc H-5), 3.95 (1H, dd, J = 8, 9 Hz, glc H-2), 4.15 (1H, t, J = 9 Hz, glc H-4), 4.23 (1H, t, J = 9 Hz, glc H-3), 4.31 (1H, dd, J = 8, 10 Hz, glc H-6), 4.48 (1H, br d, J = 10 Hz, glc H'-6), 4.74 (1H, t, J = 9 Hz, H-3), 5.00 (1H, d, J = 8 Hz, glc H-1).



 $C:M = CHCl_3:MeOH$  $C:M:W = CHCl_3:MeOH:water$ 

Chart 1

**Enzymatic Hydrolysis of 2** A mixture of **2** (37 mg) and crude naringinase (20 mg) in water (20 ml) was incubated at 37 °C for 50 h and then evaporated under reduced pressure to give a residue, which was chromatographed on a silica gel column with CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O=8:2:0.2 to provide the aglycone **2a** (3 mg). **2a**: a white powder. <sup>1</sup>H-NMR (pyridine- $d_5$ )  $\delta$ : 1.38, 1.41, 1.58 (each 3H, s, H<sub>3</sub>-12,13,15), 1.37 (1H, m, H-6), 1.55 (1H, m, H-8), 1.82 (1H, t-like, J=11 Hz, H-6), 1.95 (2H, m, H-7,9), 2.16 (1H, ddd, J=3, 12, 13 Hz, H-1), 2.33 (1H, t, J=12 Hz, H-2), 2.71 (1H, t, J=10 Hz, H-5), 2.86 (3H, m, H-2,8,9), 3.86, 3.91 (each 1H, d, J=11 Hz, H<sub>2</sub>-14), 4.79 (1H, dd, J=9, 10 Hz, H-3).

NaBH<sub>4</sub> Reduction of 1 1 (20 mg) in MeOH (10 ml) was reduced with NaBH<sub>4</sub> (100 mg), with stirring for 16 h at room temperature. Usual work-up gave the products, which were separated by silica gel column chromatography to yield a product (18.7 mg) identical with 2 in terms of  $[\alpha]_D$ , <sup>1</sup>H-and <sup>13</sup>C-NMR spectra.

Atractyloside C (3) A white powder,  $[\alpha]_{0}^{1.9} + 12.0^{\circ}$  (c = 0.95, MeOH). Negative FAB-MS m/z: 399  $[M-H]^{-}$ .  $^{1}$ H-NMR (methanol- $d_{4}$ )  $\delta$ : 0.71, 1.23, 1.25 (each 3H, s, H<sub>3</sub>-14,12,13), 1.10—1.80 (10H, m), 1.95 (1H, dd, J = 3, 12 Hz, H-3), 3.10—3.40 (6H, m), 3.66 (1H, dd, J = 5, 12 Hz, glc H-6), 3.77 (1H, m, H-2), 3.80 (1H, dd, J = 3, 12 Hz, glc H'-6), 4.47 (1H, d, J = 8 Hz, glc H-1), 4.56, 4.80 (each 1H, br s, H<sub>2</sub>-15).

Enzymatic Hydrolysis of 3 3 (10 mg) was hydrolyzed with crude naringinase in the same way as described for 1 and 2 to afford the aglycone 3a (1.2 mg), and glucose (on TLC). 3a: a white powder,  $[\alpha]_D^{16} + 31.7^\circ$  (c = 0.12, MeOH).  $^1$ H-NMR (pyridine- $d_5$ ) δ: 0.82, 1.39, 1.40 (each 3H, s, H<sub>3</sub>-14,12,13), 1.29, 1.32 (each 1H, m, H<sub>2</sub>-9), 1.40—1.60 (4H, m, H-1,6,7,8), 1.82 (1H, d, J = 13 Hz, H′-8), 1.86 (1H, d, J = 13 Hz, H-5), 2.02 (1H, br d, J = 15 Hz, H-6), 2.10 (1H, dd, J = 2, 12 Hz, H-1), 2.36 (1H, t, J = 12 Hz, H-3), 2.96 (1H, dd, J = 3, 12 Hz, H-3), 4.10 (1H, dt, J = 3, 12 Hz, H-2), 4.67, 4.91 (each 1H, br s, H<sub>2</sub>-15).

Attractyloside D (4) A white powder,  $[\alpha]_D^{17} - 15.0^\circ$  (c = 0.95, MeOH).

Negative FAB-MS m/z: 561 [M-H]<sup>-</sup>. <sup>1</sup>H-NMR (pyridine- $d_5$ )  $\delta$ : 0.66, 1.44, 1.42 (each 3H, s, H<sub>3</sub>-14,12,13), 1.10—1.50 (5H, m), 1.60 (1H, t, J=12 Hz, H-8), 1.72 (1H, d, J=12 Hz, H'-8), 1.82 (1H, d, J=13 Hz, H-5), 1.94 (1H, d, J=13 Hz, H-6), 2.15 (1H, br t, J=5 Hz, H-1), 2.33 (1H, t, J=12 Hz, H-3), 3.15 (1H, dd, J=4, 12 Hz, H'-3), 4.52, 4.73 (each 1H, br s, H<sub>2</sub>-15), 5.04, 5.05 (each 1H, d, J=7 Hz, glc H-1 × 2). Enzymatic hydrolysis of 4 in the same way as described for 3 liberated the aglycone (identical with 3a) and glucose.

Atractyloside E (5) A white powder,  $[\alpha]_0^{30} - 39.4^{\circ}$  (c = 1.00, MeOH). Positive FAB-MS m/z: 717 [M+Na]<sup>+</sup>, 537 [M-glc-H<sub>2</sub>O], 405 [m/z 537-api]. <sup>1</sup>H-NMR (pyridine- $d_5$ ) δ: 0.68, 1.39, 1.41 (each 3H, s, H<sub>3</sub>-14,12,13), 1.10—1.40 (5H, m), 1.57 (1H, t, J = 11 Hz, H-8), 1.67 (1H, d, J = 11 Hz, H'-8), 1.80 (1H, d, J = 12 Hz, H-5), 1.90 (1H, d, J = 12 Hz, H-6), 2.09 (1H, d, J = 12 Hz, H-1), 2.32 (1H, t, J = 12 Hz, H-3), 3.14 (1H, dd, J = 3, 12 Hz, H'-3), 3.80—4.70 (m), 4.73, 4.90 (each 1H, br s, H<sub>2</sub>-15), 4.96, 5.01 (each 1H, d, J = 8 Hz, glc H-1), 5.77 (1H, br s, api H-1). Atractyloside E (5) on enzymatic hydrolysis also liberated the aglycone (identical with 3a) together with glucose and apiose. A mixture of 5 (5 mg), acetic anhydride (0.3 ml) and pyridine (0.5 ml) was kept standing at room temperature and evaporated under reduced pressure to give a residue, which was subjected to silica gel column chromatography (benzene–AcOEt=2:1) to afford the acetate (3 mg) of 5, a white powder. E1-MS m/z: 766 (M – hexosyl 4Ac -H<sub>2</sub>O), 547 (pentosyl hexosyl 6Ac cation), 331 (hexosyl 4Ac cation), 259 (pentosyl 3Ac cation).

Atractyloside F (6) A white powder,  $[\alpha]_D^{19} - 99.8^\circ$  (c = 0.50, MeOH). Negative FAB-MS m/z: 825 [M-H]<sup>-</sup>, 693. <sup>1</sup>H-NMR (pyridine- $d_5$ ) δ: 0.67, 1.39, 1.46 (each 3H, s, H<sub>3</sub>-14,12,13), 1.10—1.40 (5H, m), 1.56 (1H, t, J = 12 Hz, H-8), 1.65 (1H, d, J = 12 Hz, H'-8), 1.75 (1H, d, J = 12 Hz, H-5), 1.88 (1H, d, J = 12 Hz, H-6), 2.08 (1H, d, J = 9 Hz, H-1), 2.34 (1H, t, J = 12 Hz, H-3), 3.15 (1H, t, J = 4, 12 Hz, H'-3), 3.90—4.75 (m), 4.59, 4.74 (each 1H, br s, H<sub>2</sub>-15), 4.96, 4.98 (each 1H, d, J = 7 Hz, glc H-1 × 2), 5.76,

5.78 (each 1H, d, J=2 Hz, api H-1×2). On enzymatic hydrolysis 6 also afforded the aglycone (identical with 3a) together with glucose and apiose.

Atractyloside G (7) A white powder,  $[\alpha]_D^{1.9} + 2.2^\circ$  (c = 0.045, MeOH). Negative FAB-MS m/z: 507 [M+glycerol-H]<sup>-</sup>, 415 [M-H]<sup>-</sup>. <sup>1</sup>H-NMR (pyridine- $d_5$ )  $\delta$ : 0.87, 1.44, 1.45 (each 3H, s, H<sub>3</sub>-14,12,13), 1.20—1.70 (6H, m), 1.90 (2H, m, H-5,8), 2.05 (2H, m, H-1,6), 3.90—4.40 (7H, m, sugar), 4.50 (1H, dd, J = 2, 11 Hz, glc H-6), 4.87, 5.80 (each 1H, br s, H-15), 5.06 (1H, d, J = 8 Hz, glc H-1).

Enzymatic Hydrolysis of 7 A mixture of 7 (10 mg) and crude naringinase (10 mg) in water (10 ml) was incubated at 38 °C for 16 h. Usual work-up gave an aglycone (7a) (2 mg) together with glucose (on TLC). 7a: a white powder,  $[\alpha]_D^{16} + 5.1$  (c = 0.12, MeOH). <sup>1</sup>H-NMR (pyridine- $d_5$ ) δ: 0.86, 1.40, 1.41 (each 3H, s, H<sub>3</sub>-14,12,13), 1.27 (2H, m, H<sub>2</sub>-9), 1.49 (1H, m, H-7), 1.53 (1H, m, H-6), 1.61 (1H, m, H-8), 1.68 (1H, t, J = 12 Hz, H-1), 1.82 (1H, br d, J = 11 Hz, H-8), 1.93 (1H, br d, J = 11 Hz, H-5), 2.06 (1H, br d, J = 12 Hz, H-6), 2.11 (1H, dd, J = 5, 12 Hz, H-1), 4.11 (1H, ddd, J = 5, 9, 12 Hz, H-2), 4.35 (1H, br d, J = 9 Hz, H-3), 4.97, 5.87 (each 1H, br s, H<sub>2</sub>-15).

Atractyloside H (8) A white powder,  $[\alpha]_D^{27} - 33.2^\circ$  (c = 0.50, MeOH). Positive FAB-MS m/z: 733 [M+Na]<sup>+</sup>, 553 [m/z 733 – glc – H<sub>2</sub>O+Na]<sup>+</sup>. <sup>1</sup>H-NMR (pyridine- $d_5$ ) δ: 0.69, 1.42, 1.43 (each 3H, s, H<sub>3</sub>-14,12,13), 1.12—1.63 (5H, m, H<sub>2</sub>-9, H-6,7,8), 1.74 (1H, br d, J = 14 Hz, H-1), 1.80 (1H, br d, J = 11 Hz, H'-8), 1.95 (1H, br d, J = 12 Hz, H-5), 2.03 (2H, m, H'-1,6), 3.90—4.80 (m, sugar), 4.80, 5.79 (each 1H, br s, H<sub>2</sub>-15), 4.90, 5.04 (each 1H, d, J = 8 Hz, glc H-1×2), 5.72 (1H, d, J = 2 Hz, api H-1).

Enzymatic Hydrolysis of 8 8 (10 mg) was hydrolyzed with crude naringinase as described above for 7 to give the same aglycone 7a (2 mg) as for 7, together with glucose and apiose.

**Atractyloside I (9)** Colorless needles, mp 156—158 °C,  $[\alpha]_D^{27} + 19.7^{\circ}$  (c = 1.00, MeOH). Positive FAB-MS m/z: 599  $[M + Na]^+$ , 572  $[M + H]^+$ , 415, 235. CD ( $c = 4.51 \times 10^{-4}$ , MeOH)  $[\theta]$  (nm):  $+1.66 \times 10^3$  (258), 0 (288),  $-0.69 \times 10^3$  (323). <sup>1</sup>H-NMR (pyridine- $d_5$ )  $\delta$ : 0.90, 1.36,

1.45, 2.15 (each 3H, s, H<sub>3</sub>-14,12,13,15), 1.10—1.40 (4H, m, H-6,8, H<sub>2</sub>-9), 1.72 (2H, m, H'-6, H-7), 2.23 (1H, d, J=16 Hz, H-1), 2.40 (1H, d, J=16 Hz, H'-1), 2.48 (2H, m, H-5, H'-8), 3.90—4.55 (12H, m, sugar), 5.05, 5.36 (each 1H, d, J=8 Hz, glc H-1 × 2).

**Enzymatic Hydrolysis of 9** A mixture of 3 (17 mg) and crude naringinase (24 mg) in water was incubated at 37 °C for 48 h to furnish an aglycone **9a** (6 mg) and glucose. **9a**: a white powder.  $^1\text{H-NMR}$  (pyridine- $d_5$ )  $\delta$ : 0.89 (3H, s, H<sub>3</sub>-14), 1.30—1.42 (3H, m, H-6, H<sub>2</sub>-9), 1.33 (1H, m, H-8), 1.39, 1.41 (each 3H, s, H<sub>3</sub>-12,13), 1.60 (1H, m, H-7), 1.76 (1H, br dd, J=5, 14 Hz, H'-6), 2.00 (3H, d, J=2 Hz, H<sub>3</sub>-15), 2.29 (1H, d, J=16 Hz, H-1), 2.31 (1H, m, H'-8), 2.38 (1H, br d, J=13 Hz, H-5), 2.26 (1H, d, J=16 Hz, H'-1).

Acknowledgements The authors are grateful to Prof. O. Tanaka, Hiroshima University, for providing crude naringinase, and to Mr. S. Setoguchi, Yoshitomi Pharmaceutical Co., Ltd. for facilities for X-ray measurement.

## References and Notes

- a) R. Kasai, M. Suzuo, J. Asakawa, and O. Tanaka, *Tetrahedron Lett.*, 1977, 175; b) K. Tori, S. Seo, Y. Yoshimura, H. Arita, and Y. Tomita, *ibid.*, 1977, 179.
- P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J-P. Declercq, and M. M. Woolfson, "A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data," Univs. of York, England, and Louvain, Belgium, 1982.
- C. P. Bahi, M. R. Parthasarathy, and T. R. Seshadri, *Tetrahedron*, 24, 6231 (1968).
- 4) J. K. Gawronski, Tetrahedron, 37, 3 (1981).