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CLERODANE DITERPENOIDS FROM *TEUCRIUM* AND *AJUGA* PLANTS

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Key Word Index—*Ajuga chamaepitys*; *Teucrium polium*; *T. asiaticum*; Labiatae; diterpenoids; neo-clerodane derivatives; X-ray analysis; 3-(3'-acetoxy)-14-hydro-15-hydroxyajugapitin; 19-acetylgnaphalin; teuflin; teucrin A; auropolin.

Abstract—A new clerodane diterpenoid, chamaepitin has been isolated from *Ajuga chamaepitys*. The previously known clerodanes, 19-acetylgnaphalin, auropolin, teucrin A and teuflin, have been isolated from *Teucrium* species (*T. polium* subsp. *belion*, *T. polium* subsp. *capitatum* and *T. asiaticum*) collected in Majorca. X-ray diffraction analysis on crystals of auropolin has allowed the assignment of configuration at C-20 as *S* for this compound.

INTRODUCTION

As part of our ongoing search for diterpenoid compounds from Mediterranean plants, with potential insect antifeedant activity, we have now investigated *Ajuga chamaepitys* and several *Teucrium* species, collected in Majorca.

From *A. chamaepitys*, we [1] and B. Rodriguez and coworkers [2] have isolated ajugapitin (**1**) and other related structures (**2**–**4**) that exhibited high antifeedant activity against larvae of Egyptian cotton leaf worm, *Spodoptera littoralis* [3]. In the present communication, we report on the isolation from this plant of a new clerodane diterpenoid of the above series, chamaepitin (**5**).

RESULTS AND DISCUSSION

Chamaepitin (**5**), isolated as an amorphous solid, had molecular formula $C_{31}H_{46}O_{13}$ (*m/z* 608[M − H_2O]$^+$) and its IR spectrum revealed absorptions attributable to free hydroxyl (3450 cm^{-1}) and ester (1740 and 1240 cm^{-1}) groups. Furthermore, the presence of three acetate groups was inferred from the ^{1}H and ^{13}C NMR spectra. As shown in Tables 1 and 2, from comparison with the spectral data of related clerodane structures, it was ascertained that two of these groups are attached at C-6 and C-18 and the third one is a substituent at C-3 of the 2-methylbutyryloxy moiety. This 3-acetoxy-2-methylbutyric ester function exhibited the following NMR absorptions: ^{1}H NMR δ1.18 (CH_3, *d*, *J* = 7.24 Hz), 1.22 (CH_3, *d*, *J* = 6.4 Hz), 2.38 (CH, *dd*, *J* = 12.0 and 4.0 Hz) and 5.06 (CHO, *br*); ^{13}C NMR δ172.2, 82.8, 61.1, 16.4 and 12.6. All the other signals of the above spectra agreed with the structure 3-(3'-acetoxy)-14-hydro-15-hydroxyajugapitin for compound **5**. However, it is noteworthy that the appearance of two doublets at δ5.77 and 5.81 (1H, *d*, *J* = 4.5 Hz) attributable to acetal proton H-16 suggested the occurrence of an epimeric mixture at this site. This suggestion was also confirmed by the duplication of signals in the ^{13}C NMR spectrum (see Table 2). In accord with the above assignments, CrO_3-pyridine treatment of compound **5** afforded the corresponding 2,15-dioxo-derivative **6** as an oil with molecular formula $C_{31}H_{42}O_{13}$ (*m/z* 562[M − AcOH]$^+$). The IR spectrum of compound **6** revealed the presence of a γ-lactone moiety (1780 cm^{-1}) and contained a broad carbonyl absorption (1740 cm^{-1}). There was no absorption for hydroxyl groups. In addition, its ^{1}H NMR spectrum exhibited essentially the same signals as those of **5**, except for the disappearance of H-2 and H-15 absorptions, and the pattern corresponding to H-3 and H-16, which now appeared as a singlet at δ5.92 and a doublet (*J* = 6.0 Hz) at δ6.08, respectively.

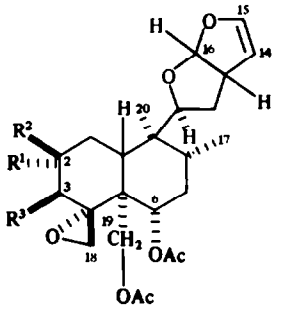
T. polium subsp. *capitatum*, *T. polium* subsp. *belion* and *T. asiaticum* collected in Majorca contained only previously known clerodane diterpenoids. Thus, from *T. polium* subsp. *capitatum* we isolated 19-acetylgnaphalin (**7**) [4] and auropolin (**8**) [5], from *T. polium* subsp. *belion* compound **7** and teucrin A (**9**) [6], and from *T. asiaticum* compound **8** and teuflin **10** [7]. All the above compounds were characterized by chemical and spectral means and, in some cases, by comparison with authentic samples.

It is noteworthy that, in contrast to previous authors [5], we have isolated auropolin (**8**) in crystalline form, mp 170–172° (EtOAc–EtOH), $[\alpha]_D^{20}$ = +26.0°($CHCl_3$; *c* 0.3281), and thus, the C-20 configuration could be studied by X-ray diffraction analysis (Fig. 1).

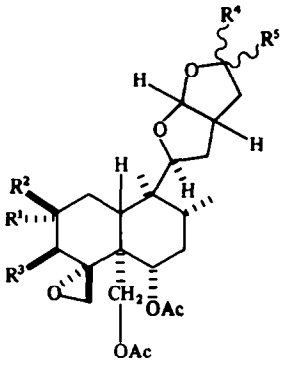
Recently, the validity of using NOE experiments for determination of the C-12 and C-20 configurations in neo-clerodane derivatives has been confirmed [8]. However, the application of this method to compound **8** by irradiation of the Me-17 protons gave no enhancement of the H-20 signal. Conversely, X-ray diffraction analysis established the configuration at C-20 of auropolin as *S*, in agreement with previous data for related neo-clerodane diterpenoids isolated from *Teucrium* genus [8].

EXPERIMENTAL

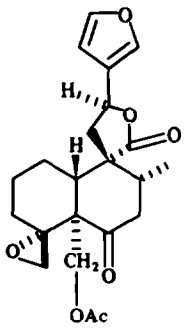
Mps (Kofler apparatus) are uncorr. ^{1}H and ^{13}C NMR: 200 (Varian XL200) and 20.15 MHz, respectively, $CDCl_3$, TMS int.



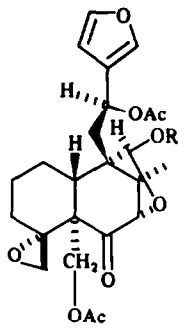
1 Ajugapitin R^1 = OH; R^2 = H; R^3 = OCO(Me)CHEt



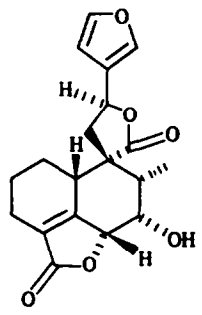
		R^1	R^2	R^3	R^4	R^5
2	15 - Ethoxy - 14 - hydroajugapitin	HO	H	EtCH(Me)COO	H	OEt
3	14 - Hydro - 15 - hydroxyajugapitin	HO	H	EtCH(Me)COO	H	OH
4	14,15 - Dihydroajugapitin	HO	H	EtCH(Me)COO	H	H
5	Chamaepitin	HO	H	MeCH(OAc)CH(Me)COO	H	OH
6		—O—		MeCH(OAc)CH(Me)COO	—O—	



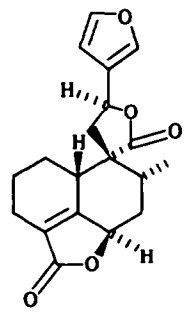
7 19 - Acetylgnaphalin



8 Auropolin (R = H)
11 20 - Acetylauropolin (R = OAc)



9 Teucrin A



10 Teuflin

We adopt here the clerodane numbering proposed by J. W. Rowe ('The common and systematic nomenclature of cyclic diterpenes', cf. The Chemical Society Specialist Periodical Reports 'Terpenoids and Steroids' **1**, 124) showing the biogenetic relationship with the labdane skeleton rather than that one used in previous papers based on clerodin numbering (Sim, G. A., Hamor, T. A., Paul, I. C. and Monteath Robertson, J. (1961) *Proc. Chem. Soc.* 75)

standard. Assignments of ^{13}C chemical shifts were made with the aid of off-resonance and noise-decoupled spectra. The NOE experiment was performed on a thoroughly degassed sample of 20-acetylauropolin (**11**) in $CDCl_3$.

EIMS (direct inlet method), 70 eV; CC: silica gel 60 (70–230 mesh; Merck), silica gel $HF_{254+366}$ (Merck) and Al_2O_3 90 [70–230 mesh; Merck; activity I (Brockmann scale)].

A. chamaepitys was collected in Vilanna (Girona, Spain), and *Teucrium* plants were collected in Majorca (Spain); voucher specimens were deposited in the Departamento de Química Orgánica Biológica, C.S.I.C. (Barcelona, Spain) and identified by Joan Fisse.

Table 1. ^{1}H NMR spectral data of clerodane diterpenoids **5**, **6**, **8** and **11***

H	5	6	8	11
2	3.60 *br*	—	—	—
3	5.18 *d*	5.92 *s*	—	—
6	4.75 *dd*	4.75 *dd*	—	—
7	—	—	4.15 *s*	4.18 *s*
11	4.07 *dd*	4.09 *dd*	—	—
12	—	—	5.87 *t*	5.86 *dd*
14	—	—	6.44 *m*	6.42 *m*
15	5.48 *dd*	—	7.41 *m*	7.43 *m*
16	5.81 *d*	6.08 *d*	7.45 *m*	7.43 *m*
16′	5.77 *d*	—	—	—
17	0.87 *d*	0.92 *d*	1.20 *d*	1.16 *d*
18	2.18; 2.77 AB	2.72; 2.90 AB	3.05 *dd*; 2.40 *d*	3.03 *dd*; 2.36 *d*
19	4.30; 4.70 AB	4.58; 4.90 AB	4.90; 5.00 AB	4.81; 5.24 AB
20	0.98 *s*	1.05 *s*	5.30 *d*	6.12 *s*
MeCOO	2.11 *s*	2.13 *s*	2.09 *s*	2.09 *s*
	1.99 *s*	2.05 *s*	2.05 *s*	2.09 *s*
	1.90 *s*	1.97 *s*		2.05 *s*

J (Hz): **5** H-3 = 9.9, H-6 = 11.0, 5, H-11 = 11.0, 5, H-15 = 10.5, 5.2, H-16 = 4.5, H-16′ = 4.5, H-17 = 4.0, H-18 = 12.0, H-20 = 7.0; **6** H-6 = 11.2, 4.9, H-11 = 11.0, 4.8, H-16 = 6.0, H-17 = 4.1, H-18 = 12.0, H-20 = 6.4; **8** H-12 = 6.5, H-17 = 7.2, H-18 = 4.8, 2.4 and H-18 = 4.8, H-19 = 11.5, H-20 = 3.8; **11** H-12 = 7.6, 5.6, H-17 = 7, H-18 = 5.2, 2.0 and H-18 = 5.2, H-19 = 11.6.

*Recorded at 200 MHz (**6**, **8**, **11**) or 80 MHz (**5**) in $CDCl_3$, TMS as int. standard.

Table 2. ^{13}C NMR spectra data for clerodane diterpenoids **5** and **8** (20.15 MHz, $CDCl_3$)

C	5	8	C	5	8	C	5	8
1	30.0	21.2	11	83.2	31.5	$CH_3\underline{C}HCOO$	172.2	
2	72.7	24.7	12	32.2	62.4	$CH_3\underline{C}HCOO$	61.1	
3	71.3	31.7	13	40.1, 40.0	125.3	$\underline{C}H_3CHCOO$	12.6	
4	62.8	62.6	14	33.3, 33.2	108.8	$\underline{C}H_3\underline{C}H(OAc)$	82.8	
5	45.6, 45.5	52.8	15	98.6	143.7	$\underline{C}H_3CH(OAc)$	16.4	
6	32.8	204.2	16	109.1, 107.2	140.1	$(O\underline{C}OCH_3)$	171.0	
7	33.1	90.9	17	13.7	99.6	$(OCO\underline{C}H_3)$	21.0	
8	35.7, 35.5	46.5	18	43.5, 43.4	15.4	$CH_3\underline{C}OO$	171.1	171.3
9	41.0	53.6	19	61.4	49.1		170.0	170.2
10	42.2, 42.1	51.3	20	16.5, 16.4	63.1	$\underline{C}H_3COO$	20.9	21.1
							20.8	21.1

The previously known compounds were identified by conventional methods and by comparison with data already described in the literature.

Extraction and isolation of diterpenoids from A. chamaepitys. Dried and finely powdered whole plants (400 g) were extracted with Et_2O (4 l) at 35° for 1 week. The solvent was evapd to yield a gum (11.6 g) which was treated with Me_2CO to precipitate the accompanying waxes. After filtration, the solvent was evapd to yield a residue (9.25 g) which was fractionated by dry CC, over silica gel 60 (180 g), eluting with 600 ml hexane–EtOAc (5:1), 400 ml hexane–EtOAc (5:2, 5:3, 5:4, 1:1, 1:2), 800 ml EtOAc and 800 ml MeOH. As previously described [1], diterpenoid **2** was eluted with hexane–EtOAc (1:2), and a fraction enriched in diterpenoids **3** and **5** with EtOAc. Further purification by successive CC, over silica gel HF and Al_2O_3 gel, eluting with hexane–EtOAc (1:1, 1:2 and 0:1) yielded finally 14-hydro-15-hydroxyajugapitin (**3**, 107 mg) and 3-(3′-acetoxy)-14-hydro-15-hydroxyajugapitin (**5**, 80 mg).

14-Hydro-15-hydroxyajugapitin (**3**). IR ν_{max}^{KBr} cm^{-1}: 3450, 1740, 1240, 1150, 1070, 1020, 970; MS *m/z* (rel. int.): 550 [M − H_2O]$^+$ (10), 449 (2), 438 (2), 339 (10), 325 (21), 265 (6), 248 (6), 218 (14), 205 (10), 200 (11), 189 (12), 187 (26), 171 (13), 159 (13), 113 (6), 111 (51) (tetrahydrofuranofuran fragment ion), 107 (10), 85 (56), 83 (85), 81 (18), 69 (15), 57 (100), 55 (15).

Chamaepitin (**5**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3450, 1740, 1240, 1130, 1120, 1070, 970; ^{1}H NMR: see Table 1; ^{13}C NMR: see Table 2; MS *m/z* (rel. int.): 608 [M − H_2O]$^+$ (0.6), 590 (1), 449 (2), 388 (2), 383 (3), 339 (3), 325 (1), 311 (2), 263 (3), 248 (3), 218 (10), 205 (4), 200 (7), 189 (5), 187 (11), 171 (5), 159 (6), 113 (3), 111 (23) (tetrahydrofuranofuran fragment ion), 85 (50), 83 (100), 81 (9), 69 (7), 57 (7), 55 (12).

2,5-Dioxoderivative (**6**). A soln of **5** (41 mg) in C_5H_5N (2 ml) was added to a mixture of CrO_3 (123 mg) in 2 ml C_5H_5N and the mixture was stirred for 22 hr. Then H_2O (15 ml) was added and the suspension was extracted with EtOAc (4 × 10 ml). The solvent was evapd at 40° yielding a crude mixture of **5** and **6** which

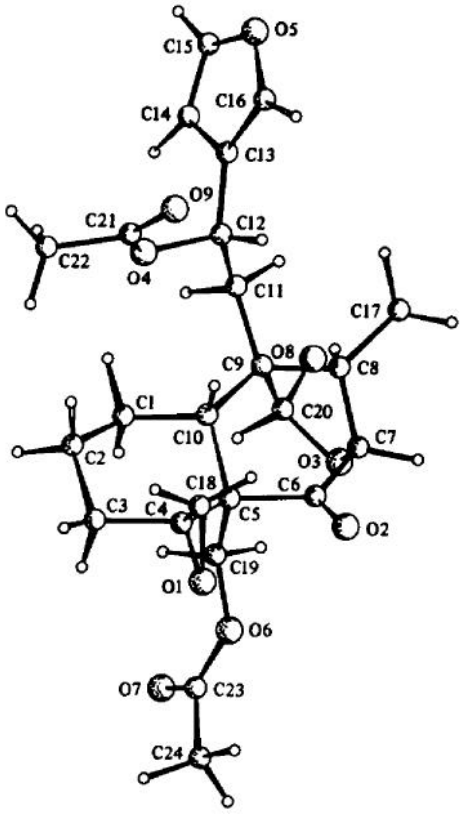


Fig. 1. Perspective view of the absolute configuration of auropolin 8.

was purified by CC over silica gel HF and eluted with hexane–EtOAc (1:2) to yield **6** (10 mg), $[\alpha]_D^{20}$ + 14.5 ($CHCl_3$, *c* 2.1); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1780 (γ-lactone), 1740 (ketone group), 1240 (ester groups); ^1H NMR: see Table 1; MS *m/z* (rel. int.): 562 $[M - AcOH]^+$ (0.1), 421 (5), 420 (12), 360 (2), 234 (3), 217 (2), 200 (2), 187 (5), 181 (3), 175 (2), 143 (52), 135 (1), 127 (9) (oxohexahydrofuranofuran fragment ion), 111 (2), 85 (3), 83 (100), 81 (6), 69 (3), 57 (4), 55 (10), 43 (67). (Found: C, 59.79; H, 7.07. $C_{29}H_{40}O_{11}$ requires: C, 59.86; H, 6.81%.)

Extraction and isolation of diterpenoids from Teucrium *species.* Dried and finely powdered aerial parts of *T. polium* subsp. *capitatum* (10.94 kg) were extracted with Me_2CO (4 l) at room temp. for 1 week. Filtration and evapn of the solvent yielded a gum (46.34 g) which was subjected to CC over silica gel 60 (800 g, deactivated with 15% H_2O). Elution with hexane–EtOAc (1:1, 1:1, 1:2 and 0:1) gave a mixture of two compounds. This mixture was subjected to further silica gel CC yielding auropolin (**8**, 270 mg) and 19-acetylgnaphalin (**7**, 26 mg).

The aerial parts of *T. polium* subsp. *belion* (1 kg) and *T. asiaticum* (0.90 kg) were treated as above, to give 19-acetylgnaphalin (**7**, 81 mg) and teucrin A (**9**, 37 mg) from the first plant and teuflin (**10**, 10 mg) and auropolin (**8**, 50 mg) from the second.

Auropolin (**8**). Mp 170–172° (from EtOAc–EtOH); $[\alpha]_D^{20}$ + 26.0° ($CHCl_3$; *c* 0.3281); IR ν_{max}^{KBr} cm^{-1}: 3440 (OH), 3120, 1505, 875 (furan ring), 1740, 1240 (COOR) 1715 (C=O), 1380, 1050; ^1H NMR: see Table 1; ^{13}C NMR: see Table 2; MS *m/z* (rel. int.): 402 $[M - AcOH]^+$ (12), 360 (13), 342 (3), 314 (13), 313 (17), 296 (13), 295 (21), 285 (18), 283 (36), 260 (20), 255 (17), 239 (10), 233 (19), 227 (14), 219 (18), 205 (10), 203 (19), 191 (23), 184 (23), 175 (40), 163 (54), 161 (45), 145 (39), 135 (20), 121 (29), 111 (24), 105 (16), 95 (46), 94 (62), 81 (41), 43 (100), 55 (13). (Found: C, 62.26; H, 6.81. $C_{24}H_{30}O_9$ requires: C, 62.33; H, 6.54%.)

20-Acetylauropolin (**11**). A soln of auropolin **8** (28 mg) in C_5H_5N (0.6 ml) and Ac_2O (0.6 ml) was allowed to stand for 6 hr at room temp. Then MeOH (1 ml) was added and after 10 min, volatile components were evapd, yielding a solid (24 mg) which crystallized from EtOAc–hexane. Mp 219–222° (from EtOAc–hexane); $[\alpha]_D^{20}$ + 56.6° ($CHCl_3$; *c* 0.492); IR ν_{max}^{KBr} cm^{-1}: 3120, 1505, 875 (furan ring), 1740, 1230 (COOR and C=O), 1370, 1050; ^1H NMR: see Table 1; MS *m/z* (rel. int.): 504 $[M]^+$ (6), 444 (15), 432 (23), 431 (74), 384 (1), 284 (19), 283 (15), 266 (14), 218 (27), 203 (23), 191 (31), 190 (31), 185 (13), 175 (79), 163 (22), 161 (18), 145 (19), 137 (28), 123 (13), 121 (15), 105 (9), 95 (24), 94 (13), 81 (24), 69 (8), 55 (8), 43 (100 base peak). (Found: C, 61.70; H, 6.30. Calc. for $C_{26}H_{32}O_{10}$: C, 61.90; H, 6.39%.)

X-Ray analysis of auropolin (**8**). Compound **8**, $C_{24}H_{30}O_9$, by slow evapn from EtOH–EtOAc soln crystallized in space group $P2_12_12_1$, with a = 8.605(4), b = 15.669 (7), c = 17.117(5)Å, V = 2308(Å^3), Z = 4.

A single crystal (0.17 × 0.21 × 0.23 mm) was mounted on an Enraf–Nonius CAD-4 automated diffractometer. Cell parameters were derived from the setting angles of 25 reflections with $4° < \theta < 11°$. Intensity data were collected using the ω-2θ scan technique with graphite monochromatized MoKα radiation. θ_{max} = 25°, h = 0, 10; k = 0, 18; l = 0, 20. The reference reflections were measured every hr and revealed no significant decay (variation < 3%). Lorentz and polarization corrections were applied to the 2325 unique observed reflections and the 763 with $I > 2.5\sigma(I)$ were used in the refinement of the structure. Intensities were not corrected for absorption or extinction.

The application of the direct methods program [9] MULTAN 11/84 for structure determination failed, due mainly to the poor quality of the crystal. However, the structure was solved by introduction of the known skeleton of 20-oxoauropolin [5] in the ROTSEARCH program [10]. The refinements were carried out by weighted Fourier synthesis and full matrix least squares [11]. Due to the small number of reflections, only the temp. factors of the oxygen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and introduced in the last stage of the refinement. The function minimized in the refinement was $w(|F_o| - |F_c|)^2$ where $w = 1/(\sigma^2(F) + 0.00017F^2)$, and $\sigma(F)$ was derived from counting statistics. Final R and Rw were 0.092 and 0.083, respectively. Parameters refined n = 179 $(\Delta/\sigma)_{max}$ = 1.25; max. and min. heights in final difference Fourier syntheses were 0.24 and 0.25 eÅ^3. Additional computer programs used were XANADU [12] and PLUTO [13].

Fig. 1 shows the perspective view of the absolute configuration of auropolin **8** and the atom numbering of the crystal structure; the bond distances and angles are of normal value.

Final atomic coordinates and equivalent temperature factors are listed in Table 3; anisotropic thermal parameters, hydrogen atom positions, F_o–F_c structure factors, selected torsion angles, asymmetry parameters and least squares mean-planes have been deposited with the British Library Lending Division. Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

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Table 3. Positional ($\times 10^3$) and equivalent isotropic thermal parameters ($Å^2$) for non-H atoms with e.s.d.'s. in parentheses

	X	Y	Z	Beq($Å^2$)
O1	943 (2)	189 (1)	771 (1)	5.7
O2	1165 (2)	300 (1)	700 (1)	5.6
O3	1056 (1)	356 (1)	512 (1)	3.9
O4	558 (2)	509 (1)	672 (1)	3.8
O5	591 (2)	783 (1)	604 (1)	7.9
O6	991 (2)	140 (1)	619 (1)	6.2
O7	882 (2)	47 (1)	542 (1)	8.1
O8	906 (2)	451 (1)	442 (1)	9.2
O9	613 (2)	571 (1)	785 (1)	5.5
C1	628 (2)	324 (1)	614 (1)	3.5
C2	570 (3)	277 (1)	685 (1)	5.3
C3	676 (3)	209 (1)	718 (1)	5.4
C4	847 (2)	241 (1)	726 (1)	3.6
C5	903 (2)	281 (1)	649 (1)	2.9
C6	1074 (3)	318 (1)	650 (1)	3.6
C7	1105 (2)	383 (1)	588 (1)	3.5
C8	1013 (2)	461 (1)	610 (1)	2.8
C9	850 (2)	429 (1)	576 (1)	3.3
C10	790 (2)	359 (1)	630 (1)	2.3
C11	734 (2)	501 (1)	562 (1)	3.6
C12	685 (2)	556 (1)	634 (1)	3.8
C13	630 (3)	643 (1)	611 (1)	4.2
C14	511 (3)	663 (2)	551 (1)	6.2
C15	496 (4)	747 (2)	555 (2)	7.8
C16	673 (3)	716 (2)	641 (1)	5.6
C17	1080 (3)	543 (1)	575 (1)	4.3
C18	891 (2)	270 (1)	802 (1)	4.6
C19	902 (2)	211 (1)	584 (1)	4.3
C20	900 (3)	388 (1)	499 (1)	5.0
C21	538 (3)	525 (1)	745 (1)	4.0
C22	392 (3)	480 (1)	777 (1)	6.8
C23	963 (3)	66 (2)	599 (1)	4.8
C24	1036 (3)	−5 (2)	644 (1)	5.8

$$Beq = \frac{8}{3}\pi^2 U_{ij} a_i a_j^* a_j^* .$$

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