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DIFFERENT OXIDATION PATHWAYS WITH VARIOUS MnO_2 TYPES: ANOMALOUS REACTION WITH GIBBERELLIC ACID

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Abstract—The oxidation of gibberellic acid (**1**) with neutral manganese dioxide prepared according to Mancera *et al.*, involves the free carboxylic group and gives rise to three anomalous products which correspond to oxidative decarboxylation (**3**, **4**) or lactonization (**5**). Optimal conditions for a normal allylic oxidation of **1** have been found using alkaline MnO_2 prepared according to Attenburrow *et al.* in acetone which gives yields of keto acid (**2**) up to 56%.

The manganese dioxide oxidation of gibberellic acid (**1**) and its methyl ester (**1a**) is known to afford the corresponding conjugated enones: the keto acid (**2**)[1,2] or its methyl ester (**2a**).[2,3] Thus, the neutral manganese dioxide prepared according to Mancera *et al.*[4] transforms the hydroxy ester **1a** into the keto ester **2a** in 70% yield (in dioxane, 80 hr at 20–25°); the oxidation of gibberellic acid itself with the same agent is reported to give the keto acid **2** in 20% yield.[2] When we tried to apply this procedure to the preparation of sufficient amounts of keto acid **2** it was found that the yield of the latter did not exceed 5–6% while three new neutral compounds arising from the anomalous oxidation could be isolated.

The oxidation of **1** with neutral MnO_2 in dioxane or in acetone affords the following new compounds: (a) the keto lactone $C_{18}H_{18}O_4$ (**3**), m.p. 231–232°, yield ~0·2%; (b) a hydroxy lactone $C_{18}H_{20}O_4$ (**4**), m.p. 195–198°, $[\alpha]_D$ + 124·5°, yield 3–4,5%; (c) a hydroxy dilatone $C_{19}H_{20}O_6$ (**5**), m.p. 285–289°, $[\alpha]_D$ + 138·8°, yield 9–13%. The recovery of the starting acid **1** even after 200 hr of oxidation was not less than 50%.

The structure of the main reaction product, dilactone **5**, is deduced from the following evidence. The IR spectrum of **5** displays in the region of CO absorbtion only one rather broad γ-lactonic band centred at 1770 cm^{-1}. On prolonged acetylation **5** affords the corresponding diacetate, $C_{23}H_{24}O_8$ (**5a**), in the IR spectrum of which two separate bands of γ-lactonic absorbtion (1780 and 1765 cm^{-1}) are observed. The presence of two lactonic rings in the molecule of **5** is further confirmed by the comparison of the CD of **5** ($[\theta]_{250}$ + 800°, $[\theta]_{227}$ −6700°, in dioxane) with that of the related monolactone **1a** ($[\theta]_{250}$ + 400°, $[\theta]_{228}$ − 3800°, in dioxane; *cf* Meguro *et al.*[5]); the intensity of the lactonic absorbtion at 227–228 nm in the case of **5** is nearly twice as high as in **1a**. The NMR spectra of **5** and **5a** show that the allylic function —HC=CH—CH(OR)— and the Me group in the ring A remain unaffected as well as the exocyclic methylene group in the ring D and the *trans*-system of protons at C-5 and C-6. The position of the second lactonic ring in the molecule of **5** follows from the presence of an one-proton signal at δ 5·61 ppm (in d_5-pyridine) which must correspond to the hydrogen at C-15; in the NMR spectrum of diacetate **5a** the signal of this proton appears at 5·37 ppm as a doublet (J = 1·2 c/s) due to the coupling with one of two methylene protons at C-17. Therefore, the NMR spectra of **5** and **5a** indicate that the C—O linkage of the newly formed lactonic ring is in an allylic position to the Δ^{16} double bond. On hydrogenation over 5% $Pd/CaCO_3$ in the presence of piperidine dilactone **5** absorbs two moles of hydrogen and gives an amorphous lacto acid (**6**) which was characterized by its crystalline methyl ester (**6a**). Since it is known that the addition of piperidine completely prevents hydrogen from attacking the exocyclic Δ^{16} double

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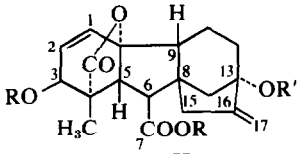
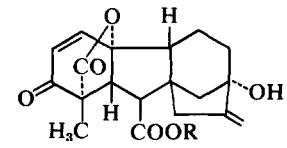
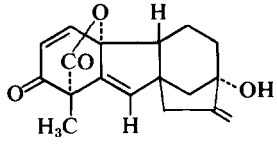


1: R = R′ = H
1a: R = CH_3, R′ = H
1b: R = H, R′ = CH_3CO(or Ac)



2: R = H
2a: R = CH_3



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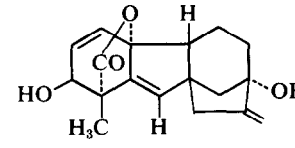

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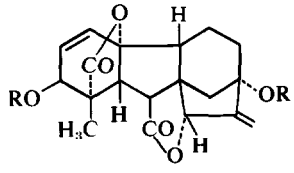
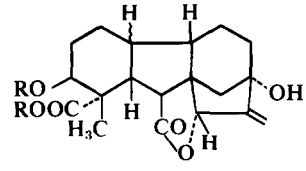
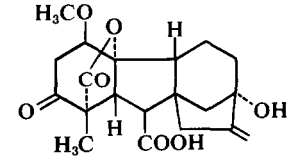


5: R = H
5a: R = CH_3CO



6: R = H
6a: R = CH_3



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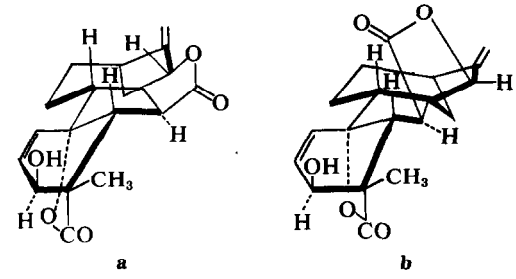
bond[6], the 7 → 15 lactonic group in the molecule of **6** must remain untouched. Indeed, the NMR spectrum of **6a** in addition to the signals of olefinic protons at C-17 retains the signal of the proton attached to C-15 (δ 5·30 ppm, 1H).

A reaction analogous to the transformation of **1** into **5** takes place upon manganese oxidation of gibberellic acid diacetate (**1b**) in acetone. In this case the above-mentioned diacetate **5a** can be obtained, although in low yield (~5%). Two points may be deduced from this observation. In the first place, the oxidative lactonization does not require the presence of a free hydroxyl group. Secondly, in the course of oxidation the configuration at C-3 remains unaffected although the mechanism advanced by Pratt[7] does not exclude the possibility of inversion at the allylic centre in the case of free alcohols such as **1**. Since the oxidation of **1** and its diacetate **1b** proceeds similarly both in the air and under argon, the participation of molecular oxygen in the oxidative lactonization appears unlikely.

The stereochemistry of dilactones **5** and **5a** at the newly created asymmetric centre (C-15) was not determined. However, the consideration of molecular Dreiding models shows that among two possible stereoisomers only the 15(R)-compound (Fig 2a) is relatively unstrained while in its 15(S)-counterpart the 7 → 15 lactonic bridge is drastically distorted (Fig 2b). On this ground dilactone **5** is tentatively formulated as 15(R)-isomer.



a b

Fig 2.

The second anomalous product from the manganese oxidation of **1** may be formulated as **4** on the basis of its elementary analysis and IR, UV, NMR and mass spectra. The NMR spectrum of this hydroxy lactone displays the signals belonging to the allylic —HC=CH—CH—OH system while the IR and UV spectra do not exhibit any absorbtion characteristic for conjugated enones. The presence of an additional double bond follows from the NMR spectrum of **4** where a one-proton signal appears at δ 5·66 ppm; isolated character of this trisubstituted double bond can be seen from the IR and UV spectra of **4**. The presence of two hydroxy groups is evidenced by the shift of the molecular ion peak from *m/e* 300 to *m/e* 302 upon exchange with MeOD.

Finally, the minor product of oxidation, the keto lactone **3**, reveals in its IR and UV spectra the presence of the conjugated enone grouping in the ring A (ν 1690 and 1610 cm^{-1}, $\epsilon_{233} = 6200$, $\epsilon_{371} = 85$). The same product was obtained upon manganese oxidation of **4** in acetone (TLC data).

Seeking for optimal conditions in regard to the desired keto acid **2** other modified procedures of the manganese dioxide oxidation of gibberellic acid (**1**) have been tested under standard conditions (5 mg substrate **1** with 25 mg MnO_2 in 1·5 ml solvent for 90 hr at room temp under argon). Thus, neutral manganese dioxide in different solvents also after activation via azeotopic removal of water with benzene following the procedure of Goldman[8] showed a very low oxidation rate with mainly unchanged **1** in the TLC. Much better results have been obtained using alkaline prepared manganese dioxide of Attenburrow *et al*[9] where a clean oxidation process took place. Under the above mentioned standard conditions in different solvents the following oxidation rates could be estimated from TLC results: acetone, acetonitrile > tetrahydrofuran > dimethylformamide > dimethylsulfoxide, pyridine. For preparative scale the procedure with alkaline MnO_2 in acetone was found to be the best which gives after silicagel chromatography the desired keto acid **2** in yields between 35 and 56% besides starting gibberellic acid (**1**). In contrast to the results with neutral manganese dioxide prepared according to Mancera *et al.* neither the products of oxidative decarboxylation (**3** and **4**) nor of lactonization (**5**) could be detected in this case. If methanol has been used instead of acetone in the final extraction of MnO_2 (Experimental) a minor product of m.p. 242–245° (dec) and $[\alpha]_D^{17}$ +75·9° (in ethanol) was isolated in 11% yield. The structure of this compound is deduced as methoxy acid **7** from the following evidence: In the mass spectrum the molecular ion peak appears at *m/e* 376 and indicates the uptake of 1 molecule methanol. On the other hand IR and UV data show no longer enone absorption but saturated ketone with the positive Cotton effect of 3-carbonyl gibberellins at 295 nm (a = +155) in the ORD curve. The NMR spectrum of **7** (in d_6-DMSO) exhibits besides a three-proton singlet at 1·00 (18-H_3) a further one at 3·25 indicative for a 1-OMe group, and a one-proton signal at 3·82 (ppm) for the 1-hydrogen. The coupling pattern of the latter with $J_{AX} = 5$ and $J_{BX} = 2$ cs, respectively, indicates an equatorial C_1-proton and therefore 1β-position of the OMe group.[10] The methyl ester of **7** has been shown to be identical with an authentic specimen prepared earlier in an independent way.[2,10]

The observed formation of the anomalous oxidation products **3**, **4** and **5** with neutral manganese dioxide prepared according to Mancera *et al.* in contrast to the results obtained with alkaline Attenburrow MnO_2 preparation is a drastic example of qualitative difference in the reaction pathways of various manganese dioxide types.

In contrast to the results obtained starting with gibberellic acid (**1**) the oxidation of methyl ester **1a** with neutral as well as alkaline MnO_2 affords only enone **2a** in good yields. This implies that only in the presence of the free carboxylic group qualitatively different reaction pathways take place which point to a different absorption behaviour of the acid **1** on the surface of both used manganese dioxide preparations. Generally it is known that when an allylic hydroxy group in a cyclic system is quasi-axial, its oxidation with MnO_2 takes place more slowly[11] (or even does not take place at all[12]) which is also the case in the Δ^1-3β-hydroxy gibberellic system [3] with a quasi-axial hydroxyl at C-3. In the special situation of the oxidation of free gibberellic acid with neutral MnO_2 in comparison to alkaline Attenburrow MnO_2 this already slow allylic oxidation process is nearly completely supressed so that anomalous oxidative decarboxylation and lactonization (which was earlier observed for *ortho*-substituted benzoic acids[13]) may become predominant leading to **4** and **5**, respectively.

The formation of dilactone **5** can be explained as the result of hydroxylation with manganese dioxide[14,15] at an available allylic position (i.e. at C-15) which is followed by dehydration and the formation of the 7 → 15 lactonic ring. However, another possibility, i.e. that the formation of **4** and **5** results from two different ways of stabilization of the initially formed carboxy-radical (Figs 3a and 3b) appears more tempting.

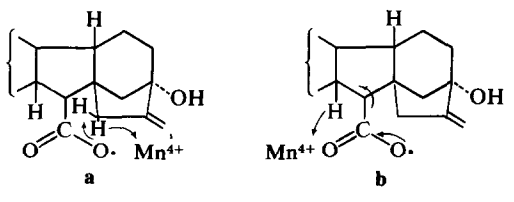


Fig 3.

EXPERIMENTAL

M.ps are corrected. IR spectra in KBr-pellets if not otherwise stated, with UR-10 instrument (Zeiss, Jena). NMR spectra (δ(ppm) values): Varian HA-100 instrument. Mass spectra: MX 1303 instrument with all-glass inlet system, at 190–230° or electron-attachment mass spectrograph of the Research Institute Manfred v. Ardenne. Chromatography: silica gel KSK (120–150 mesh) or silica gel Woelm for partition chromatography and neutral alumina (grade II/III, 150–180 mesh). Specific rotations: in pyridine if not otherwise stated. Circular dichroism (*c* 0·01 mole/l, in dioxane): Spectropol-1 instrument (France). ORD measurements: JASCO-ORD/UV-S instrument in MeOH. The chromatographically pure gibberellic acid had m.p. 233–234° and $[\alpha]_D$ +86°. Its acetylation according to a known procedure[3] gave **1b**

which was chromatographed on silica gel and recrystallized from EtOAc–hexane: m.p. 233–236°, $[\alpha]_D$ +169° (Lit.[3]; m.p. 186–187°, $[\alpha]_D$ + 176°). The neutral MnO_2 was prepared according to Mancera *et al.*[4] from $KMnO_4$ (grade "chemically pure", standard 4527-48) and $MnSO_4$ (grade "pure", standard 435-41), the alkaline MnO_2 according to Attenburrow *et al.*[9] from $KMnO_4$ and $MnSO_4 \cdot 4H_2O$ (grade "for analysis"). The drying of MnO_2 was carried out at 120° for 48 hr and at 130° for 7 hr, respectively.

Gibberellic acid (**1**) *and neutral manganese dioxide*

(a) To a soln of **1** (10·0 g) in 1200 ml of freshly distilled acetone neutral MnO_2[4] (90 g) was added and the suspension was shaken for 153 hr at 20–23° in a dark-glass vessel. After filtration the ppt was thoroughly washed with acetone and the combined acetone soln was evaporated and chromatographed on 400 ml of silica gel treated with 114 ml of phosphate buffer (pH 6·2). Elution with benzene–CH_2Cl_2 (6:4) gave enone **3** (14·5 mg), m.p. 231–233° (from acetone), MW 298 (mass spectrometry). IR spectrum: 3540, 3100, 3050, 1765, 1690, 1655, 1610, 1210, 1155, 1050, 945 and 845 cm^{-1}; UV spectrum: 233 (ϵ 6,200), 338 (ϵ 140), 351 (ϵ 132) and 371 (ϵ 85) nm. Elution with benzene–CH_2Cl_2 (2:8) gave **4** (250 mg), m.p. 195–198° (from EtOAc), $[\alpha]_D^{25}$ + 124·5° (c = 0·45); IR spectrum: 3420, 3055, 1759, 1665, 1380, 1175, 1110, 1050, 902, 895 cm^{-1}; NMR spectrum (in d_6-acetone): 1·28 (3H, s), 3·98 (1H, d, J = 4 c/s), 4·90 (1H), 5·66 (1H), 5·82 and 6·23 (2H, AB-system, J_{AB} = 9 c/s: additional splitting at 5·82 ppm with J = 4 c/s). Mass spectrum: M^+ 300 (0·37); *m/e* 282 (0·15), 256 (0·34), 255 (0·72), 254 (0·80), 239 (0·37), 238 (0·83), 237 (1·0), 223 (0·27), 209 (0·31), 199 (0·18), 185 (0·32), and 155 (0·19). (Found: C, 72·06; H, 6·76. $C_{18}H_{20}O_4$ requires: C, 71·98; H, 6·71%). Elution with pure CH_2Cl_2 afforded small amount of **2**. Further elution with CH_2Cl_2–EtOAc (9:1) gave **5** (1·040 g), m.p. 285–289° (from acetone), $[\alpha]^{25}$ + 138·8° (c = 0·36); this compound is poorly soluble in most solvents except pyridine; IR spectrum: 3510, 3420, 3385, 3065, 1770, 1675, 1645, 1390, 1280, 1215, 1155, 1005, 915 and 900 cm^{-1}; NMR spectrum (in d_5-pyridine): 1·66 (3H, s), 3·18 and 3·38 (2H, AB-system, J_{AB} = 9 c/s), 4·38 (1H, d, J = 4 c/s), 4·79 (1H), 5·27 (1H), 5·61, (1H), 6·00 and 6·28 (2H, AB-system, J_{AB} = 9 c/s: additional splitting at 6·28 ppm with J = 4 c/s). Mass spectrum: M^+ 344 (1·0), *m/e* 326 (0·01), 315 (0·01), 300 (0·03), 298 (0·03), 282 (0·02), 271 (0·07), 255 (0·08), 209 (0·08), 155 (0·04) and 135 (0·08); CD: $[\theta]_{250}$ = +800°, $[\theta]_{227}$ = −6700°. (Found: C, 66·01; H, 6·10. $C_{19}H_{20}O_6$ requires: C, 66·27; H, 5·85%). On chromatoplates with silica gel **5** gives pink or purple colouring when sprayed with conc H_2SO_4 and heated to 80° for 5–10 min. On prolonged treatment with Ac_2O–pyridine (20–23°, 40 days) followed by chromatography on silica gel **5** affords the corresponding diacetate (**5a**), m.p. 288–290° (from acetone); IR spectrum: 1780, 1765, 1740, 1680, 1380, 1370, 1255, 1235, 1190, 1150, 1020, 900 cm^{-1}; NMR spectrum (in d_5-pyridine): 1·46 (3H, s), 1·83 (3H, s), 1·88 (3H, s), 3·22 and 3·42 (2H, AB-system, J_{AB} = 9 c/s), 4·87 (1H), 5·25 (1H, d, J = 1·2 c/s), 5·37 (1H, d, J = 1·2 c/s), 5·51 (1H, J = 4 c/s), 5·81 and 6·38 (2H, AB-system, J_{AB} = 10 c/s; additional splitting at 5·81 ppm with J = 4 c/s); Mass spectrum: M^+ 428.

(b) Gibberellic acid (2·0 g) in pure dioxane (150 ml) was oxidized with neutral MnO_2 (18 g) as described above. After 175 hr the products were chromatographed on 90 ml of silica gel to afford **4** (58 mg, m.p. 195–198°) and **5** (218 mg, m.p. 285–289°).

Gibberellic acid diacetate (**1b**) *and neutral manganese dioxide*

Diacetate **1b** (495 mg) and neutral MnO_2 (5·2 g) in 75 ml acetone were shaken for 200 hr at 20–23°; the products were chromatographed on 40 ml of silica gel treated with phosphate buffer (pH 6·2). Elution with CH_2Cl_2 gave a crystalline mixture of oxidation products (89 mg) and then unreacted **1b** (390 mg). The former was carefully washed with small portions of acetone and afforded 14·5 mg of pure **5a**, m.p. 287–289°, identified with the previously described specimen by its TLC behaviour as well as by IR and mass spectra. The acetone filtrate was evaporated and chromatographed on alumina (5 g). Elution with benzene–chloroform (2:8) gave an unidentified crystalline substance (15·1 mg) with m.p. 148–160°; IR spectrum: 1780, 1740, 1665, 1375, 1240, 1230, 905 cm^{-1}; MW 444 (mass spectrometry). (Found: C, 62·18; H, 6·39 $C_{23}H_{24}O_9$ requires: C, 62·16; H, 5·44%). Further elution with the same solvent ratio afforded additional amounts of **5a** (9 mg), m.p. 286–288°, M^+ 428.

Selective hydrogenolysis of dilactone **5**

Dilactone **5** (190 mg) was dissolved in a mixture of pyridine (2 ml), THF (50 ml) and piperidine (2 ml) and hydrogenated over 5% Pd/$CaCO_3$ until the uptake of H_2 ceased (~2·05 moles H_2). The products were chromatographed on 10 ml of buffered (pH 6·2) silica gel without separation into acidic and neutral fractions. Elution with $CHCl_3$–EtOAc (3:7) afforded **6** (37 mg) as an amorphous solid foam. IR spectrum: 3340–3200, 1750, 1710 cm^{-1}; MW 348 (mass spectrometry). On treatment with diazomethane **6** gives the corresponding methyl ester (**6a**), m.p. 249–253° (from acetone), MW 362 (mass spectrometry), IR spectrum: 3415, 1770, 1730, 1200, 1120, 895 cm^{-1}; NMR spectrum: (in d_6-acetone): 1·35 (3H, s), 3·63 (3H, s), 4·05 (1H), 4·90 (1H), 5·20 (1H) and 5·30 (1H).

Gibberellic acid (**1**) *and alkaline manganese dioxide*

To a soln of **1** (10·0 g) in 1170 ml of freshly distilled acetone alkaline MnO_2 prepared from 122 g $MnSO_4 \cdot 4H_2O$ in 130 ml 40% NaOH and 106 g $KMnO_4$ in 660 ml water following the procedure of Attenburrow *et al.*[9] was shaken for 153 hr at 20° under argon. After filtration the ppt was thoroughly washed with 2 l acetone and the combined solns evaporated. The oily residue (10·12 g) was absorbed on celite (20 g) and chromatographed on 400 g of silica gel Woelm. Elution with CH_2Cl_2 (1:1) afforded 5·559 (56%) crystalline **2**, m.p. 227–229° (from acetone–hexane) and $[\alpha]_D$ +60·7° (c = 0·595 in EtOH). (Lit.[1]: m.p. 214–216° $[\alpha]_D$ +71°; Lit.[2]: m.p. 205–206° (from EtOAc), $[\alpha]_D$ +46·4°). Further elution with the same eluents gave a mixture of **2** and starting **1** (0·454 g). Elution with CH_2Cl_2–EtOAc (4:6, 2:8, and 1:9) and pure EtOAc yielded **1** (1·79 g). In another oxidation experiment starting from 10 g **1** after filtration the MnO_2 ppt was washed with MeOH instead of acetone, and the oily residue obtained chromatographed on silicagel as above. In this case elution with CH_2Cl_2–EtOAc (1:1) afforded at first 1·05 g (11%) of **7**, m.p. 242–245° (from acetone–hexane), and $[\alpha]_D^{17}$ +75·9° (c = 0·435 in EtOH), IR spectrum: 3410, 3090, 1760, 1692, 1650, 1095, 1028, 907 cm^{-1}; UV spectrum: 290 (ϵ 60); NMR spectrum (in d_6-DMSO): 1·00 (3H, s), 2·54 (1H, d, J = 10 c/s), 3·10 (1H, d, J = 10 c/s), 3·25 (3H, s), 3·82 (1H, q, J_{AX} = 5, J_{BX} = 2 c/s), 4·76 and

5·02 (2H); Mass spectrum (electron-attachment mass spectrograph, $T_v = 100°$): M^+ 276 (0·85), 358 (0·67), 344 (0·32), 331 (0·42), 326 (0·41), 300 (1·00), 288 (0·36), 271 (0·44), 257 (0·57), 243 (0·42), 231 (0·44), 201 (0·66), 189 (0·72), 163 (0·63), 136 (0·78) and 121 (0·55). ORD: $[\theta]_{315} = +6000$; $[\theta]_{266} -9475$ (a = +155). Further elution with CH_2Cl_2–EtOAc (1:1, 4:6) yielded 3·34 g (34%) of **2** and subsequently 0·52 g of a mixture of **2** and **1**. Elution with CH_2Cl_2–EtOAc 2:8, and pure EtOAc gave starting acid **1** (3·2 g).

Addendum. For reasons of brevity the nomenclature names of compounds obtained in this work were omitted. We propose the names 20-nor-10α,13α,15α-trihydroxy-ent-gibberell-16-ene-7,19-dioic acid 19 → 10/7 → 15 dilactone (**5**) and 7,20-bisnor-10α, 13α-dihydroxy-ent-gibberell-5,16-dien-19-oic acid 19 → 10 lactone (**4**) for the representatives of both structural types.

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