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New generation of enantiomerically pure *N*-α-carboxyalkylglycolurils

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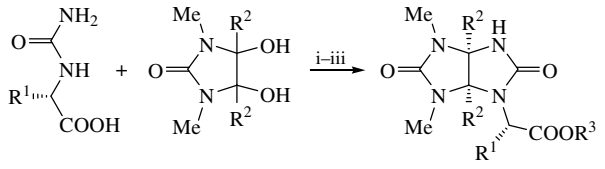
The title compounds have been synthesised by the α-ureidoalkylation of (*S*)-*N*-carbamoyl-α-amino acids with 1,3-dimethyl- and 1,3-dimethyl-4,5-diphenyl-4,5-dihydroxyimidazolidin-2-ones.

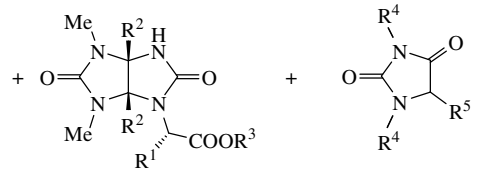
2,4,6,8-Tetraalkyl-2,4,6,8-tetraazabicyclo[3.3.0]octane-3.7-diones (2,4,6,8-tetraalkylglycolurils) possess the highest psychotropic activity among bicyclic bisureas.[1] Furthermore, there are compounds of this class that are currently at various stages of adoption to medical practice, including Mebicarum, a well-known day-time tranquillizer.[2] The incorporation of a carboxypropyl moiety at a glycoluril nitrogen atom gives rise to anxiolytic and antihypoxic properties (even in racemates) comparable to similar effects of Mebicarum.[3] Therefore, the simultaneous incorporation of carboxyalkyl and alkyl moieties into a glycoluril molecule may enhance these types of activity. On the other hand, racemic glycolurils with phenyl groups at the C(1) and C(5) bridging atoms exhibit another type of activity, *viz*., they affect the monooxygenase system of liver,[4] though they are not very efficient. Thus, it was of interest to synthesise glycolurils that combine alkyl, phenyl and carboxyalkyl substituents in a molecule. As a rule, only one enantiomer in racemic pharmaceutical compounds is useful.[5] This study aims at synthesising glycolurils of a new type whose molecules contain *N*-alkyl, phenyl and (*S*)-α-carboxyalkyl groups in various combinations.



1a–e **2a,b** **3a–c, 4a–d**

1: **a** R^1 = Me
b R^1 = Et
c R^1 = Pr
d R^1 = Pr^i
e R^1 = Bn

2: **a** R^2 = H
b R^2 = Ph



3′a–c, 4′a,c,d **5a–f**

3, 3′: **a** R^1 = Me, R^2 = R^3 = H
b R^1 = Et, R^2 = R^3 = H
c R^1 = Pr, R^2 = R^3 = H

4, 4′: **a** R^1 = Me, R^2 = Ph, R^3 = Me
b R^1 = Et, R^2 = Ph, R^3 = Me
c R^1 = Pr^i, R^2 = Ph, R^3 = Me
d R^1 = Bn, R^2 = Ph, R^3 = Me

5: **a** R^4 = H, R^5 = Et
b R^4 = H, R^5 = Me
c R^4 = H, R^5 = Pr
d R^4 = H, R^5 = Pr^i
e R^4 = H, R^5 = Bn
f R^4 = Me, R^5 = H

Scheme 1 *Reagents and conditions*: i, 1 mol **2a**:0.5 mol HCl, H_2O or H_2O + Pr^{i}OH, 85–90 °C, 3 h (diastereoselective synthesis of **3a–c**); ii, 1 mol **2a**:1 mol HCl, H_2O or H_2O + Pr^{i}OH, 85–90 °C, 3 h (diastereospecific synthesis of **3c**); iii, 1 mol **2**:1 mol HCl, MeOH or MeOH + Pr^{i}OH, reflux, 2 h (diastereoselective synthesis of **4a**,**c**,**d** or diastereospecific synthesis of **4b**).

Table 1 Dependence of the yields and diastereomeric ratios of glycolurils on the amount of HCl used.

Reagents	Amount of HCl (molar equiv.)	Diastereomeric ratio **3**:**3′** and **4**:**4′**	Yield (%)
1a, 2a	0.5	**3a**:**3′a**, 1:1	25
	1	**3a**:**3′a**, 1.5:1	20
1b, 2a	0.5	**3b**:**3′b**, 1.5:1	37
	1	**3b**:**3′b**, 3.5:1	25
1c, 2a	0.5	**3c**:**3′c**, 5:1	10
	1	Stereoisomer **3c**	8
1a, 2b	0.5	**4a**:**4′a**, 1:1	88
	1	**4a**:**4′a**, 2.5:1	80
1b, 2b	0.5	Stereoisomer **4b**	91
	1	Stereoisomer **4b**	83
1d, 2b	0.5	**4c**:**4′c**, 1:1	16
	1	**4c**:**4′c**, 3:1	10
1e, 2b	0.5	**4d**:**4′d**, 1:1	74
	1	**4d**:**4′d**, 2:1	70

We have previously obtained enantiomerically pure *N*-α-carboxyalkylglycolurils containing neither phenyl nor alkyl substituents by diastereoselective and diastereospecific cyclocondensations of N-nonsubstituted 4,5-dihydroxyimidazolidin-2-one (DHI) with (*S*)- and (*R*)-*N*-carbamoyl-α-amino acids under acidic catalysis conditions.[6,7] Therefore, to synthesise a new generation of enantiomerically pure glycolurils, we studied the α-ureidoalkylation of (*S*)-*N*-carbamoyl-α-amino acids (*N*-carbamoylalanine **1a**, *N*-carbamoyl-α-aminobutyric acid **1b**, *N*-carbamoylnorvaline **1c**, *N*-carbamoylvaline **1d** and *N*-carbamoylphenylalanine **1e**) using 1,3-dimethyl-DHI **2a** and 1,3-dimethyl-4,5-diphenyl-DHI **2b** as ureidoalkylating reagents. The reactions were carried out for 2–3 h in the presence of concentrated HCl (from 0.5 to 2 mol) at 85–90 °C in various solvents. These studies resulted in target glycolurils **3a–c** and **4a–d** (Scheme 1)† with various diastereomeric compositions (Table 1). Water or an H_2O–Pr^{i}OH mixture (1:1.5) were the best suitable solvents for synthesising glycolurils **3a–c**, while MeOH or an MeOH–Pr^{i}OH mixture (1:1) were the best solvents for obtaining compounds **4a–d**. Note that the use of MeOH in the syntheses of glycolurils **4** resulted in the methyl esters of *N*-α-carboxyalkylglycolurils **4a–d** and **4′a**,**c**,**d** due to the esterification of carboxylic groups.‡

† The configurations of the CH–CH bridging carbon atoms in the bicyclic system, *viz*., 1*R*,5*R* in the major diastereomer and 1*S*,5*S* in the minor one, was assigned by analogy with monosubstituted *N*-α-carboxyalkylglycolurils obtained previously,[6,7] based on the similarity of the ^{1}H and ^{13}C NMR spectra of compounds **3** and **4**.

The diastereomeric composition of the reaction products was determined by ^{1}H and ^{13}C NMR spectroscopy. Glycolurils **3a**,**b** and **4a**,**c**,**d** were formed as mixtures of two diastereomers **3a**,**b** and **3′a**,**b** or **4a**,**c**,**d** and **4′a**,**c**,**d**; this was observed as doubling of some proton signals. The signals of the CH protons in the amino acid moiety of the major diastereomers are shifted downfield with respect to similar signals of the minor diastereomers.

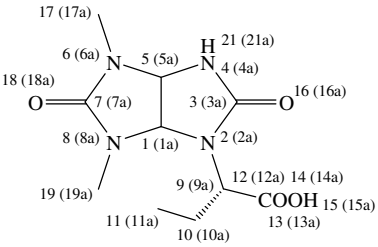


Figure 1 Atom numbering in the major and minor diastereomers of **3b + 3′b**, which is used for the assignment of the signals of protons to those of the carbon atoms based on the HSQC and HMBC spectra of these compounds. A letter 'a' at the numbers of atoms signifies the same atoms in the second isomer.

The signals in the ^{1}H and ^{13}C NMR spectra were assigned using HSQC[8] and HMBC[9] techniques. The studies were carried out for diastereomers **3b + 3′b** using [$^2H_6$]DMSO as a solvent. The HMBC spectrum shows cross peaks corresponding to the long-range interactions of the protons at C(9) or C(9a) with the carbon atoms of carbonyl groups C(3) or C(3a) and C(12) or C(12a), respectively, and with just one cyclic carbon atom C(3) or C(3a). The protons of the methyl groups at carbon atoms C(17) or C(17a) and C(19) or C(19a) display cross peaks with the corresponding carbon atom C(7) or C(7a) of the carbonyl group. The protons of the Me group at carbon atom C(19) or C(19a) manifest long-range interactions with the cyclic carbon atom C(1) or C(1a), respectively, whereas the protons of the methyl groups at C(17) or C(17a) manifest long-range interactions with carbon atom C(5) or C(5a). Based on the HSQC and HMBC spectra of compounds **3b + 3′b**, we assigned the proton signals to those of carbon atoms (Figure 1).

Analysis of the information-richest part of the spectra of the test compounds (*i.e.*, the area of the signals of the amino acid moiety CH protons at δ 3.7–4.5) shows that, depending on the structure of the starting compounds and the molar amount of HCl per mole of DHI **2a**,**b**, the ratio of diastereomers **3a** and **3′a** varies from 1:1 to 1.5:1; for **3b** and **3′b**, from 1.5:1 to 3:1; for **3c** and **3′c**, from 5:1 to 1:0; for **4a** and **4′a**, from 1:1 to 2.5:1; for **4c** and **4′c**, from 1:1 to 3:1; and for **4d** and **4′d**, from 1:1 to 2:1 (Table 1), which indicates that the reactions of DHI **2a** with (*S*)-*N*-carbamoyl-α-amino acids **1a**–**c** and of DHI **2b** with (*S*)-*N*-carbamoyl-α-amino acids **1a**,**d**,**e** occur diastereoselectively. The reaction of DHI **2a** with (*S*)-*N*-carbamoylnorvaline **1c** in the presence of 1 mol of HCl and that of DHI **2b** with *N*-carbamoyl-α-aminobutyric acid **1b** in the presence of either 0.5 or 1 mol of HCl result in one stereoisomer **3c** or **4b**, respectively.

Under conditions of the synthesis (2 mol of HCl),[2] the reactions of *N*-carbamoyl-α-amino acids **1a**–**e** and DHI **2a**,**b** result in corresponding hydantoins **5a**–**f**, which are formed as by-products due to a pinacoline-type rearrangement of DHI **2a**,**b**[10] and the cyclization of **1a**–**e**.[11] The reactions of *N*-carbamoyl-α-amino acids **1d**,**e** with DHI **2a** and (*S*)-*N*-carbamoylnorvaline **1c** with DHI **2b** under similar conditions result in hydantoins **5d**,**e** and **5c**, respectively.

‡ All the new compounds exhibited satisfactory elemental analyses, and their structures were confirmed by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker WM-250 (250 MHz), AM-300 (75.5 MHz) and DRX-500 (500 MHz) instruments. Chemical shifts were measured with reference to the residual protons of [$^2H_6$]DMSO as a solvent (δ 2.50).

Melting points were determined in a Gallenkamp instrument (Sanyo).

Commercial compounds (benzene, amino acids, KOCN, diethylthio- and dimethylureas) from Acros were used in the syntheses. The solvents were used without preliminary purification. Starting *N*-carbamoyl-α-amino acids **1a**–**e**[12,13] and DHIs **2a**,**b**[14,15] were synthesised as described in the literature.

3a/3′a (1.5:1): yield 25%, mp 248–250 °C (MeOH). ^{1}H NMR ([$^2H_6$]DMSO) δ: 5.11–5.28 (m, 2H CH–CH); diastereomer **3a**: 1.40 (m, 3H, Me), 2.72 (s, 3H, Me), 2.62 (d, 3H, Me, *J* 7.5 Hz), 4.30 (m, 1H, CH), 8.12 (s, 1H, NH); diastereomer **3′a**: 4.11 (m, 1H, CH), 7.77 (s, 1H, NH).

3b/3′b (3.5:1): yield 37%, mp 295–297 °C (MeOH). ^{1}H NMR ([$^2H_6$]DMSO) δ: 0.85 [m, 3H, Me(11 + 11a)], 1.79 [m, 2H, CH_2(10a)], 1.92 [m, 2H, CH_2(10)], 2.63 [s, 3H, Me(17a)], 2.64 [s, 3H, Me(19a)], 2.72 [s, 3H, Me(17)], 2.74 [s, 3H, Me(19a)], 3.90 [m, 1H, CH(9)], 4.13 [dd, 1H, CH(9a), *J* 5 Hz], 5.13 [m, 2H, CH–CH(5 + 5a + 1 + 1a)], 7.77 [s, 1H, NH(21)], 7.85 [s, 1H, NH(21a)]. ^{13}C{^{1}H} NMR ([$^2H_6$]DMSO) δ: 10.90 [Me(11)], 11.10 [Me(11a)], 21.51 [CH_2(10a)], 23.10 [CH_2(10)], 27.88 [NMe(17a)], 27.92 [NMe(17)], 29.68 [NMe(19a)], 30.27 [NMe(19)], 56.94 [CH(9)], 57.97 [CH(9a)], 66.13 [NCHN(5a)], 66.30 [NCHN(5)], 72.31 [NCHN(1a)], 72.44 [NCHN(1)], 158.14 [CO(7a)], 158.54 [CO(7)], 159.77 [CO(3a)], 160.02 [CO(3)], 172.49 [COOH(12)], 172.88 [COOH(12a)].

3c: yield 8%, mp 300–302 °C (MeOH), $[\alpha]_D^{20}$ +71 (*c* 1.8, MeOH). ^{1}H NMR ([$^2H_6$]DMSO) δ: 0.89 (m, 3H, Me), 1.30 (m, 2H, CH_2), 1.90 (m, 2H, CH_2), 2.65 (s, 3H, Me), 2.78 (s, 3H, Me), 4.00 (m, 1H, CH), 5.11 (s, 2H, CH–CH), 7.79 (s, 1H, NH).

3c/3′c (5:1): yield 10%, mp 298–300 °C (MeOH). ^{1}H NMR ([$^2H_6$]DMSO) δ: 0.81–0.89 (m, 3H, Me), 1.45–1.65 (m, 2H, CH_2), 1.66–2.01 (m, 2H, CH_2), 2.63 (s, 3H, Me), 2.65 (s, 3H, Me), 2.81 (s, 3H, Me), 2.82 (s, 3H, Me), 4.00 (m, 1H, CH), 4.48 (m, 1H, CH), 5.11 (s, 2H, CH–CH), 5.15 (s, 2H, CH–CH), 7.77 (s, 1H, NH), 7.85 (s, 1H, NH).

4a/4′a (2.5:1): yield 88%, mp 138–140 °C (MeOH). ^{1}H NMR ([$^2H_6$]DMSO) δ: 1.4 (d, 3H, CMe), 2.56 (s, 3H, NMe), 2.58 (s, 3H, NMe), 2.75 (s, 3H, NMe), 2.80 (s, 3H, NMe), 3.61 (s, 3H, OMe), 3.68 (s, 3H, OMe), 3.91 (dd, 1H, CH, *J* 7 Hz), 4.08 (d, 1H, CH, *J* 7 Hz), 6.73–7.17 (m, 10H, Ph), 8.45 (s, 1H, NH), 8.51 (s, 1H, NH). ^{13}C{^{1}H} NMR ([$^2H_6$]DMSO) δ: 16.00 (Me), 16.87 [Me(a)], 26.44 [NMe(a)], 26.79 (NMe), 28.78 [NMe(a)], 28.99 (NMe), 50.02 (CH), 51.27 [CH(a)], 52.29 (OMe), 83.18 [CPh(a)], 83.67 (CPh), 7.23 (CPh), 87.67 [CPh(a)], 127.53–129.26 (Ph), 33.36 (C, Ph), 133.95 [C, Ph(a)], 135.28 (C, Ph), 135.64 [C, Ph(a)], 158.28 (CO), 58.76 [CO(a)], 58.81 [CO(a)], 58.89 (CO), 71.44 (COO), 71.74 [COO(a)].

4b: yield 91%, mp 263–265 °C (MeOH), $[\alpha]_D^{20}$ +118 (*c* 2.0, MeOH). ^{1}H NMR ([$^2H_6$]DMSO) δ: 0.90–1.03 (m, 3H, CMe), 1.97–2.17 (m, 1H, CH_2), 2.24–2.43 (m, 1H, CH_2), 2.55 (s, 3H, NMe), 2.73 (s, 3H, NMe), 3.27–3.32 (m, 1H, CH), 3.61 (s, 3H, OMe), 6.80–7.17 (m, 10H, Ph), 8.40 (s, 1H, NH). ^{13}C{^{1}H} NMR ([$^2H_6$]DMSO) δ: 13.19 (Me), 26.10 (NMe), 26.52 (NMe), 28.81 (CH_2), 52.10 (OMe), 57.51 (CH), 82.95 (CPh), 87.63 (CPh), 127.40–128.49 (Ph), 133.76 (C, Ph), 135.41 (C, Ph), 158.64 (CO), 158.92 (CO), 172.48 (COO).

4c/4′c (3:1): yield 16%, mp 240–242 °C (MeOH). ^{1}H NMR ([$^2H_6$]DMSO) δ: 0.93–1.05 (m, 7H, $CHMe_2$), 2.60 (s, 3H, NMe), 2.75 (s, 3H, NMe), 2.87 (s, 3H, NMe), 2.89 (s, 3H, NMe), 3.20 (d, 1H, CH, *J* 9 Hz), 3.30 (d, 1H, CH, *J* 9 Hz), 3.44 (s, 3H, OMe), 3.51 (s, 3H, OMe), 6.77–7.25 (m, 10H, Ph), 8.37 (s, 1H, NH), 8.52 (s, 1H, NH). ^{13}C{^{1}H} NMR ([$^2H_6$]DMSO) δ: 19.38 [CMe(a)], 19.58 (CMe), 20.06 [CMe(a)], 21.10 (CMe), 25.87 [CH(a)], 26.15 (CH), 28.43 [NMe(a)], 28.83 (NMe), 29.34 [NMe(a)], 29.79 (NMe), 51.40 [OMe(a)], 51.62 (OMe), 61.95 (CH), 83.39 (CPh), 83.50 [CPh(a)], 87.59 (CPh), 88.58 [CPh(a)], 127.36–128.44 (Ph), 133.09 [C, Ph(a)], 133.40 (C, Ph), 134.53 (C, Ph), 134.19 [C, Ph(a)], 157.86 [CO(a)], 158.51 (CO), 158.68 [CO(a)], 159.16 (CO), 170.75 (COO), 171.43 [COO(a)].

4d/4′d (2:1): yield 74%, mp 175–177 °C (MeOH). ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.55 (s, 3H, NMe), 2.57 (s, 3H, NMe), 2.58 (s, 3H, NMe), 2.61 (s, 3H, NMe), 2.64–2.70 (m, 2H, CH_2), 3.58 (s, 3H, OMe), 3.65 (s, 3H, OMe), 6.98–7.33 (m, 15H, Ph), 8.53 (s, 1H, NH), 8.62 (s, 1H, NH). ^{13}C{^{1}H} NMR ([$^2H_6$]DMSO) δ: 25.41 (NMe), 26.55 [NMe(a)], 29.00 (NMe), 29.16 [NMe(a)], 35.98 (CH_2), 36.42 [CH_2(a)], 52.13 (CH), 55.61 [CH(a)], 58.63 (OMe), 62.06 [OMe(*a*)], 82.70 [CPh(a)], 82.89 (CPh), 87.49 (CPh), 87.62 [CPh(a)], 126.21–129.75 (Ph), 132.62 [C, Ph(a)], 132.93 (C, Ph), 135.02 [C, Ph(a)], 135.27 (C, Ph), 138.20 [C, Ph(a)], 138.64 (C, Ph), 158.36 (CO), 158.48 [CO(a)], 158.70 [CO(a)], 158.78 (CO), 170.64 (COO), 171.05 [COO(a)].

These results suggest that the yields and diastereoselectivity or diastereospecificity in the syntheses of glycolurils **3**, **4** are affected by both the amount of HCl added to the reaction mixture and the structures of starting DHIs **2a**,**b** and *N*-carbamoyl-α-amino acids **1a**–**e**. Increasing the amount of the acid increases the diastereoselectivity but decreases the yields of target glycolurils **3**, **4** due to an increase in the yields of hydantoins **5a**–**f**. With DHI **2a**, the yields of diastereomers **3a** + **3′a** and **3b** + **3′b** are 25% and 37%, respectively, whereas the yield of compound **3c** in the reaction with *N*-carbamoylnorvaline **1c** amounts to 8–10%. In the case of DHI **2b**, the yields of glycolurils **4a** + **4′a**, **4b** and **4d** + **4′d** are mainly in the range 74–91%; it is only in the case of *N*-carbamoylvaline **1d** that the yields of compounds **4c** + **4′c** decrease to 10–16%. We failed to separate the mixtures of diastereomers **3a** and **3′a**, **3b** and **3′b**, **4a** and **4′a**, **4c** and **4′c**, **4d** and **4′d** by crystallisation from H_2O, MeOH, Pr^iOH or their mixtures because of similar physicochemical properties of these compounds.

Thus, this study revealed that the α-ureidoalkylation of *N*-carbamoyl-α-amino acids **1a**–**e** using DHIs **2a**,**b**, both N-substituted and incorporating phenyl substituents at C(4) and C(5), as the ureidoalkylating agents can occur diastereoselectively, and also diastereospecifically in some cases. This allowed us to obtain the first representatives of enantiomerically pure glycolurils (**3c** and **4b**) and diastereomeric *N*-α-carboxyalkylglucolurils with the predomination of one of the compounds (**3a** and **3′a**, **3b** and **3′b**, **4a** and **4′a**, **4c** and **4′c**, **4d** and **4′d**) and to reveal the dependence of their yields on the amount of HCl and on the structure of the DHIs and *N*-carbamoyl-α-amino acids **1a**–**e**.

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