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— as to the identity of the inventor (Rule 4.17(i))

Published:

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- (54) **Title:** PREPARATION METHOD FOR 1-PHENYL-2,6-BIS(2-HYDROXYETHYL)IMIDAZO[1,5-C]QUINAZOLINE-3,5-DIONE AND 1-PHENYL-2,6-BIS(2-HYDROXYPROPYL)IMIDAZO[1,5-C]QUINAZOLINE-3,5-DIONE

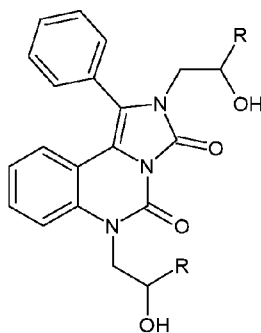


Fig. 1 where: R = -H, -CH₃

- (57) **Abstract:** This method relates to the preparation of the compound of structural formula 1, where R is a hydrogen atom -H or methyl group -CH₃ respectively, in reactions of 1-phenyl-2H,6H-imidazo[1,5-c]quinazoline-3,5-dione with formula 2 and oxiranes with formula 3 in form of ethylene oxide for R = -H or propylene oxide for R = CH₃ respectively. In the first stage, reactions are conducted in pressurized reactor, at a molar ratio of 1-phenyl-2H,6H-imidazo[1,5-c]quinazoline-3,5-dione to oxirane equal to 1 : 2, in solvent and in presence of triethylamine as catalyst, and in the second stage after the reaction is finished, catalyst and solvent are distilled off under reduced pressure, precipitated with acetone, and then the resulting compound is filtered and crystallized from ethanol. In the first step, in the case of ethylene oxide reactions are conducted at temperature of 60 ÷ 70 °C for at least 70 hours, whereas in the case of propylene oxide it is conducted at temperature of 70 ÷ 90°C for at least 90 hours. Furthermore, in the first step dimethyl sulfoxide is used as a solvent in the first step, whereas in the second step distillation of the catalyst and solvent is conducted under pressure lower than 10 mm Hg. The invention may be used as compounds having potential biological activity, starting compounds in synthesis of medicines or substrates for synthesis of other organic compounds with imidazoquinazoline ring.



Preparation method for 1-phenyl-2,6-bis(2-hydroxyethyl)imidazo[1,5-c]quinazoline-3,5-dione and 1-phenyl-2,6-bis(2-hydroxypropyl)imidazo[1,5-c]quinazoline-3,5-dione

The subject of the invention is the preparation method for 1-phenyl-2,6-bis(2-hydroxyethyl)imidazo[1,5-c]quinazoline-3,5-dione and 1-phenyl-2,6-bis(2-hydroxypropyl)imidazo[1,5-c]quinazoline-3,5-dione in form of a compound with structural formula 1 where R is a hydrogen atom -H or methyl group -CH₃ respectively, in reactions of 1-phenyl-2H,6H-imidazo[1,5-c]quinazoline-3,5-dione with formula 2 and oxiranes with formula 3 in form of ethylene oxide for R = -H or propylene oxide for R = CH₃ respectively which may be used as compounds having potential biological activity, starting compounds in synthesis of medicines or substrates for synthesis of other organic compounds with imidazoquinoline ring.

Preparation methods for bis-substituted derivatives of 2H,6H-imidazo[1,5-c]quinazoline, including 1-phenyl-2H,6H-imidazo[1,5-c]quinazoline-3,5-dione, in reactions with ethylene oxide and propylene oxide in presence of acid or basic catalysts has not yet been disclosed in any patent description. The only information that can be found include synthesis of derivatives of other compounds with imidazoquinoline unit, such as in the publication of patent description No WO2009138796A2 (and the following analogues: EP2297159B1, CN102066379A, RU2010151143A, AU2009247797A1, CA2723858A1, US2011152298A1, KR20110017873A, JP2011521910A, MX2010012540A, NZ589108A). In the above-mentioned publication, derivatives of imidazo[2,1-b]quinazolin-2-one were obtained and substituted with halogen atoms as well as alkyl, hydroxyl, nitro, cyano, amino or alkoxy groups. In the subsequent publication of the patent description No WO2009138788A1 (and the following

analogues: RU2010151142A, AU2009247789A1, CA2723857A1, CN102066341A, EP2297116A1, JP2011520858A, KR20110007247A, MX2010012541A, NZ589106A, US2011130413A1) and No WO2009138789A1 (and the following analogues: US2011130405, KR20110006726A, 5 AU2009247790A1, CA2724213A1, CN102076687, JP2011520859A), derivatives of derivatives of anagrelide (6,7-dichloro-1,5-dihydro-imidazo[2,1-b]quinazolin-2(3H)-one) substituted by groups analogous to imidazo[2,1-b]quinazolin-2-one were obtained. Anagrelide is applied in medicine and pharmacy due to its biological activity. Among the compounds described, the above-mentioned 10 publications however list neither 1-phenyl-2,6-bis(2-hydroxyethyl)-6H-imidazo[1,5-c]quinazoline-3,5-dione nor 1-phenyl-2,6-bis(2-hydroxypropyl)-6H-imidazo[1,5-c]quinazoline-3,5-dione.

The use of ethylene oxide in the preparation of diols in reaction with heterocyclic compounds with nitrogen atoms was disclosed in publication of 15 British patent description No GB1290729A (and the following analogues: GB1290729A, AT293433B, AT296331B, AT298807B, AT300826B, BE741506A, BE750116A4, BE759863A4, BE762253A4, CA920598A1, CA939349A1, CA962680A2, CH521970A, CH523278A, CH523279A, CH525894A, CH549045A, CH552005A, CH552007A, CH557398A, 20 CH559727A5, CS160115B2, CS160116B2, DE1954503A1, DE1966743A1, DE2020091A1, DE2059623A1, DE2104279A1, ES373376A1, ES379472A2, ES385362A1, ES385363A1, ES386181A2, ES387744A2, FR2022997A1, FR2077627A2, FR2080885A2, FR2085582A2, GB1290728A, GB1291187A, GB1304770A, GB1334461A, GB1334462A, IT954103B, IT989564B, 25 JPS5034031B1, JPS5034032B1, JPS5416508B1, NL6916903A, NL7006624A, NL7017771A, NL7101233A, SE359544B, SE391924B, SU372815A3, SU398028A3, SU407448A3, SU526288A3, US3629263A, US3631221A, US3772326A, US3828045A, US4060525A, US4161594A, US4227005A, YU245070A, ZA7003049A, ZA7007994A, ZA7100501A). Among the

compounds described, the above-mentioned publication does not however list 1-phenyl-2,6-bis(2-hydroxyethyl)-6H-imidazo[1,5-c]quinazoline-3,5-dione or 1-phenyl-2,6-bis(2-hydroxypropyl)-6H-imidazo[1,5-c]quinazoline-3,5-dione. In these syntheses methods of diols, there is however the need to use excessive amount of oxirane due to very large losses of this substrate in the reaction. Syntheses with use of ethylene oxide with a boiling point of 10.7 °C were conducted under reflux condenser, initially at temperature of 50 ÷ 60 °C and after exothermic effect which occurs during the reaction has subsided at temperature of 90 °C which resulted in evaporating large amount of oxirane used.

Preparation method for 1-phenyl-2,6-bis(2-hydroxyethyl)imidazo[1,5-c]quinazoline-3,5-dione and 1-phenyl-2,6-bis(2-hydroxypropyl)imidazo[1,5-c]quinazoline-3,5-dione in the form of a compound with structural formula 1, where R means hydrogen atom -H or methyl group -CH₃ respectively, in reactions of 1-phenyl-2H,6H-imidazo[1,5-c]quinazoline-3,5-dione with formula 2 and oxiranes with formula 3 in form of ethylene oxide for R = -H or propylene oxide for R = -CH₃ respectively, according to the invention it is characterized by the fact that in the first stage reactions are conducted in pressurized reactor, at a molar ratio of 1-phenyl-2H,6H-imidazo[1,5-c]quinazoline-3,5-dione to oxirane ratio equal to 1:2, in solvent and in presence of triethylamine as catalyst, and in the second stage after the reaction is finished, catalyst and solvent are distilled off under reduced pressure. The resulting product is precipitated in acetone and purified by crystallization from ethanol.

Preferably in the first step, in the case of ethylene oxide reactions are conducted at temperature of 60 ÷ 70 °C for at least 70 hours, whereas in the case of propylene oxide it is conducted at temperature of 70 ÷ 90°C for at least 90 hours.

Further benefits are obtained if dimethyl sulfoxide is used as a solvent in the first step, whereas in the second step distillation of the catalyst and solvent is conducted under pressure lower than 10 mm Hg.

According to the invention, the preparation process of 1-phenyl-2,6-bis(2-hydroxyethyl)imidazo[1,5-c]quinazoline-3,5-dione and 1-phenyl-2,6-bis(2-hydroxypropyl)imidazo[1,5-c]quinazolin-3,5-dione consists in reaction of 1-phenyl-2H,6H-imidazo[1,5-c]quinazolin-3,5-dione and oxiranes, such as ethylene
5 oxide and propylene oxide. This reaction is conducted in pressurized reactor at molar ratio of the substrates equal to 1: 2, in environment of dimethyl sulfoxide, which is the best aprotic solvent of 1-phenyl-2H,6H-imidazo[1,5-c]quinazoline-3,5-dione in the presence of triethylamine as a catalyst. After the reaction is completed, catalyst and solvent are distilled under lowered pressure. The resulting
10 product is precipitated in acetone and purified by crystallization from ethanol.

The use of pressure reactors allows to conduct the reaction at high temperature without oxirane losses as it occurs in known method described in patent publication No GB1290729A. The use of ethylene oxide and propylene oxide is more beneficial than the use of appropriate chlorohydrins. Reaction with
15 chlorohydrins involves substitution of the chlorine atom through the nitrogen atom of the heterocyclic ring, whereas in basic medium, sodium or potassium chloride is formed in addition to hydroxyalkyl derivatives of azaheterocyclic compounds. However, in the method according to the invention 1-phenyl-2H,6H-imidazo[1,5-c]quinazoline-3,5-dione is added to oxiranes, but this reaction does
20 not produce any by-products which have to be removed from the reaction mixture. This eliminates laborious purification of the N-hydroxyalkyl derivatives of 1-phenyl-2H,6H-imidazo[1,5-c]quinazoline-3,5-dione from resulting salts in form of sodium or potassium chloride.

Solution according to the invention is further explained in the examples
25 and in the drawing, in which the figures 1,4 and 5, showing structural formulas, represent 1-phenyl-2,6-bis(2-hydroxyethyl)imidazo[1,5-c]quinazoline-3,5-dione for R = -H and 1-phenyl-2,6-bis(2-hydroxypropyl)imidazo[1,5-c]quinazolin-3,5-dione. Figure 2 represents 1-phenyl-2H,6H-imidazo[1,5-c]quinazoline-3,5-dione, whereas figure 3 - oxirane in form of ethylene oxide for R = -H and propylene

oxide for R = -CH₃. The numbers from 1-25 near the symbols of atoms in figures 4 and 5 represent numbers of atoms which were used below in the preparation examples in description of ¹H-NMR (proton magnetic resonance) and ¹³C-NMR (carbon magnetic resonance) spectra of the compounds to confirm their structure.

5 Example 1

In the pressurized reactor with capacity of 100 cm³, 2.77 g (10 mmol) of 1-phenyl-2H,6H-imidazo[1,5-c]quinazoline-3,5-dione, 20 cm³ of dimethyl sulfoxide, 0.1 g (1 mmol) of triethylamine and 0.88 g (20 mmol) of ethylene oxide were placed. The reaction mixture was stirred with a magnetic stirrer and heated
10 to the temperature of 70°C. Reaction was completed after 70 hours, when collected sample of reaction mixture did not reveal loss in mass on the analytical balance and the epoxide number was zero. DMSO was distilled off under reduced pressure (p = 7 mm Hg, the temperature of the liquid 65 - 110°C, temperature of vapors 68 - 72°C). The resulting products were precipitated with acetone, then
15 drained and purified by crystallization from ethanol.

1-phenyl-2,6-bis(2-hydroxyethyl)imidazo[1,5-c]quinazoline-3,5-dione with formula 1, where R = -H, was received. Product characteristics: melting point of 217 ÷ 218 ° C; IR (KBr) (IR spectrum made in the form of pellets with potassium bromide), ν = 3435 (s, OH valence), 3030 (w, CH, deformation of
20 phenyl ring), 2955 (w, -CH₂-, asymmetric valence), 2883 (w, -CH₂-, symmetric valence), 1742 (s, C=O, valence), 1053 (m, C-O-H, valence), 1660, 1612, 1509, 1445 (s, skeleton of phenyl ring), 1156 (w, C-H, flat deformation), 752, 699 (s, deformation, non-flat), 1631, 1587, 1485 (s, skeletal of quinazoline ring), 845 (m, deformation) [cm⁻¹]; ¹H-NMR (500 MHz, d₆-DMSO (deuterated dimethyl sulfoxide)), δ = 3.35 (2 H, t, -N-CH₂-, J_{20,21} = 5.51 Hz), 3.47 (2H, t, -CH₂-OH, J_{20,21} = 6.24 Hz), 3.64 (2 H, t, -N-CH₂-, J_{22,23} = 5.51 Hz), 4.10 (2H, t, -CH₂-OH, J_{22,23} = 6,24 Hz), 4.81 (1 H, t, -OH, J_{O,21} = 5.42 Hz), 4.90 (1 H, t, -OH, J_{O,23} = 5.42 Hz), 6.72 (1 H, d, J_{8,9} = 8.07 Hz), 6.80 (1 H, t, J_{10,11} = 7.45 Hz), 7.21 (1 H, t, J_{9,8} = 7.25 Hz), 7.29 (1 H, d, J_{11,10} = 8.09 Hz) 7.54 (2 H, m), 7.62 (3 H, m); ¹³C-NMR

(d₆-DMSO), δ = 147.90 (C₃), 145.10 (C₅), 134.79 (C₇), 131.05 (C₁₇), 129.94 (C₁₆, C₁₈), 129.44 (C₁₅ i C₁₉), 128.26 (C₁₄), 127.88 (C₉), 125.29 (C₁₁), 122.48 (C₁₀), 121.13 (C₈), 117.75 (C₁), 114.01 (C₁₃), 111.84 (C₁₂), 57.75 (C₂₁), 56.49 (C₂₃), 44.12 (C₂₂), 43.15 (C₂₀), [ppm]; AE (elemental analysis), %N_{calculated} = 11.57, %N_{determined} = 11.41, %C_{calculated} = 65.75, %C_{determined} = 65.60, %H_{calculated} = 5.24, %H_{determined} = 5.08; UV (ultraviolet spectrum), 224, 264, 335 [nm].

Example 2

In the pressurized reactor with capacity of 100 cm³, 2.77 g (10 mmol) of 1-phenyl-2H,6H-imidazo[1,5-c]quinazoline-3,5-dione, 20 cm³ of dimethyl sulfoxide, 0.2 g (2 mmol) of triethylamine and 1.16 g (20 mmol) of propylene oxide were placed. The reaction mixture was stirred with a magnetic stirrer and heated to the temperature of 90°C. Reaction was completed after 90 hours, when collected sample of reaction mixture did not reveal loss in mass on the analytical balance and the epoxide number was zero. The next step was the same as in example 1.

1-phenyl-2,6-bis(2-hydroxypropyl)imidazo[1,5-c]quinazoline-3,5-dione with formula 1, where R = -CH₃, was received with capacity of 60%. Product characteristics: melting point of 178 ÷ 179 ° C; IR (KBr), ν = 3446 (s, O-H valence), 3032 (w, C-H, valence in the ring), 2954 (w, -CH₂-, asymmetric valence), 2882 (w, -CH₂-, symmetric valence), 1745 (s, C=O, valence), 1061 (m, C-O-H, valence), 1660, 1612, 1509, 1445 (s, skeleton of phenyl ring), 1156 (w, C-H, flat deformation), 752, 699 (s, deformation, non-flat), 1631, 1587, 1485 (s, skeletal of quinazoline ring), 845 (m, deformation) [cm⁻¹]; ¹H-NMR (500 MHz, d₆-DMSO), δ = 0.88 (3H, d, CH₃, J_{22,21} = 6.42 Hz), 1.35 (3H, d, CH₃, J_{25,24} = 6.42 Hz), 3.51 (1 H, dd, -N-CH-, J_{20AB} = 24.64 Hz, J_{20A,21} = 6.98 Hz), 3.56 (1H, dd, -CH-N, J_{20AB} = 24.64 Hz, J_{20B,21} = 6.28 Hz), 3.62 (1 H, dd, -N-CH-, J_{23AB} = 23.73 Hz, J_{23A,24} = 8.38 Hz), 3.68 (1H, dd, -CH-N, J_{23AB} = 23.73 Hz, J_{23B,24} = 7.68 Hz), 3.90 (1 H, sept., CH-OH, J_{21,22} = 6.82 Hz), 4.60 (1 H, sept., CH-OH, J_{23,24} = 6.82

Hz), 4.82 (1 H, d, -OH), 4.92 (1 H, d, -OH), 6.75 (1 H, d, $J_{10,11} = 6.16$ Hz), 7.10 (1 H, t, $J_{10,9} = 7.86$ Hz), 7.21 (1 H, d, $J_{9,8} = 7.45$ Hz), 7.32 (1 H, t, $J_{9,10} = 7.86$ Hz), 7.52 (2 H, m), 7.63 (3 H, m); ^{13}C -NMR (d_6 -DMSO), $\delta = 148.10$ (C_3), 144.81 (C_5), 134.12 (C_7), 131.82 (C_{17}), 131.00 (C_{16} , C_{18}), 129.81 (C_{15} , C_{19}), 129.21 (C_{14}), 128.36 (C_{13}), 127.85 (C_9), 122.37 (C_{10}), 120.82 (C_{11}), 118.21 (C_1), 114.92 (C_8), 112.61 (C_{12}), 64.26 (C_{24}), 63.15 (C_{21}), 49.02 (C_{23}), 47.92 (C_{20}), 20.72 (C_{25}), 20.60 (C_{22}), [ppm]; AE, $\%N_{\text{calc.}} = 11.37$, $\%N_{\text{determ.}} = 11.30$, $\%C_{\text{calc.}} = 65.03$, $\%C_{\text{determ.}} = 65.29$, $\%H_{\text{calc.}} = 6.28$, $\%H_{\text{determ.}} = 6.20$.

The invention may be used as compounds having potential biological activity, starting compounds in synthesis of medicines or substrates for synthesis of other organic compounds with imidazoquinazoline ring.

Claims

1. Preparation methods of 1-phenyl-2,6-bis(2-hydroxyethyl)imidazo[1,5-c]quinazoline-3,5-dione and 1-phenyl-2,6-bis(2-hydroxypropyl)imidazo[1,5-c]quinazoline-3,5-dione in form of compound with structural formula 1, where R means hydrogen atom -H or methyl group -CH₃ respectively, in reactions of 1-phenyl-2H,6H-imidazo[1,5-c]quinazoline-3,5-dione with formula 2 and oxiranes with formula 3 in form of ethylene oxide for R = -H or propylene oxide for R = -CH₃ respectively, according to the invention it is **characterized in that** in the first stage reactions are conducted in pressurized reactor, at a molar ratio of 1-phenyl-2H,6H-imidazo[1,5-c]quinazoline-3,5-dione to oxirane ratio equal to 1:2, in solvent and in presence of triethylamine as catalyst, and in the second stage after the reaction is finished, catalyst and solvent are distilled off under reduced pressure, precipitated with acetone, and then the resulting compound is filtered and crystallized from ethanol.

2. According to claim 1, the method is **characterized in that** in the first step, in the case of ethylene oxide reactions are conducted at temperature of 60 ÷ 70 °C for at least 70 hours.

3. According to claim 1, the method is **characterized in that** in the first step, in the case of propylene oxide reactions are conducted at temperature of 70 ÷ 90 °C for at least 90 hours.

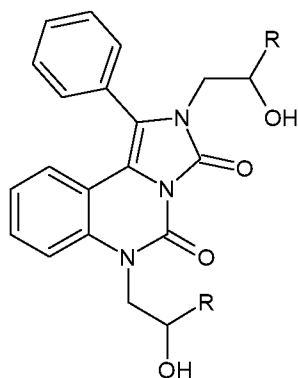
4. According to claim 1, 2 or 3, the method is **characterized in that** in the first step dimethyl sulfoxide is used as the solvent.

5. According to claim 1, 2, 3 or 4, the method is **characterized in that** in the second step distillation of the catalyst and solvent is conducted under pressure lower than 10 mm Hg.

6. According to claim 1, 2, 3, 4 or 5, the method is **characterized in that** product is precipitated with acetone.

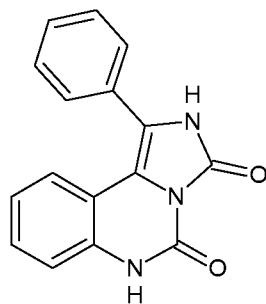
7. According to claim 1, 2, 3, 4, 5 or 6, the method is **characterized in that** product is purified by crystallization from ethanol.

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where: R = -H, -CH₃

Fig. 1



where: R = -H, -CH₃

Fig. 2

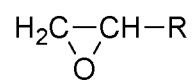


Fig. 3

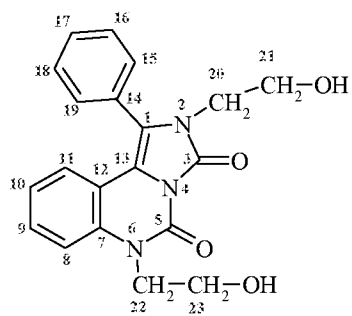


Fig. 4

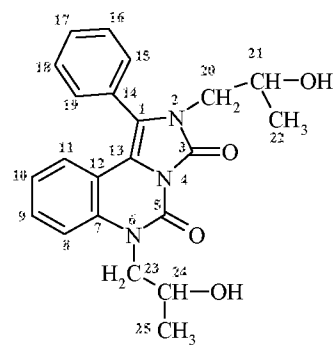


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No

PCT/PL2015/050037

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07D487/14 C07D487/12
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 679 681 A (HABERMEIER JUERGEN ET AL) 25 July 1972 (1972-07-25) column 2, line 63 - column 3, line 15; column 6, lines 20-64; column 8, line 74 - column 9, line 25; claims -----	1-7
Y	US 3 629 263 A (BATZER HANS ET AL) 21 December 1971 (1971-12-21) starting from column 7, "Manufacture of the starting compounds", e.g. Example B at column 8, lines 21-50 or Example G at column 10, lines 21-75 -----	1-7
Y	GB 1 334 462 A (CIBA GEIGY AG) 17 October 1973 (1973-10-17) page 1, lines 25-43; page 2, lines 1-41; examples -----	1-7

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/PL2015/050037

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3679681	A	25-07-1972	AT 294118 B	10-11-1971
			AT 297020 B	10-03-1972
			BE 744846 A1	23-07-1970
			CH 546242 A	28-02-1974
			DE 2003016 A1	30-07-1970
			GB 1289772 A	20-09-1972
			JP S5111116 B1	08-04-1976
			JP S5133907 B1	22-09-1976
			US 3679681 A	25-07-1972

US 3629263	A	21-12-1971	AT 293433 B	11-10-1971
			AT 296331 B	10-02-1972
			AT 298807 B	25-05-1972
			BE 741506 A	11-05-1970
			BE 750116 A4	09-11-1970
			CH 523278 A	31-05-1972
			CH 523279 A	31-05-1972
			CH 557398 A	31-12-1974
			DE 1966743 A1	15-11-1973
			DE 2020091 A1	19-08-1971
			FR 2022997 A1	07-08-1970
			FR 2077627 A2	29-10-1971
			GB 1290728 A	27-09-1972
			GB 1290729 A	27-09-1972
			GB 1291187 A	04-10-1972
			NL 6916903 A	13-05-1970
			NL 7006624 A	03-08-1971
			SE 391924 B	07-03-1977
			US 3629263 A	21-12-1971
			US 3631221 A	28-12-1971
			US 3772326 A	13-11-1973
			US 4227005 A	07-10-1980

GB 1334462	A	17-10-1973	NONE	
