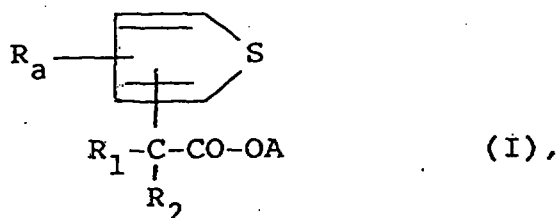


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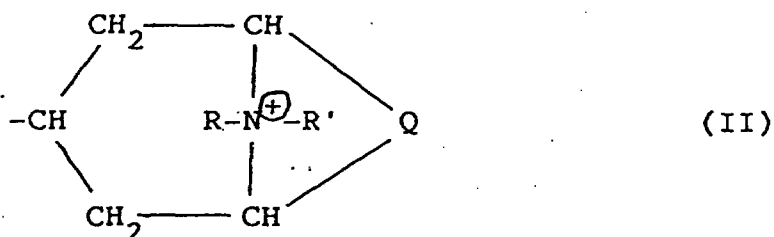
The invention relates to novel thienylcarboxylates of amino alcohols and their quaternary products and to the preparation of the novel compounds and their use as active ingredients in medicaments.

The novel compounds correspond to the formula



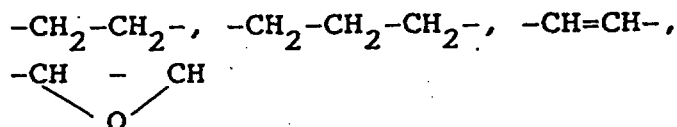
in which

A represents the group



wherein

Q represents one of the double-bonding groups



and R denotes an optionally halogen-substituted or hydroxy-substituted C₁-C₄ alkyl radical, R' denotes a C₁-C₄ alkyl radical and R and R' together may also form a C₄-C₆ alkylene radical and one equivalent of an anion (X⁻) opposes the positive charge of the N-atom,

R₁ represents a thienyl, phenyl, furyl, cyclopentyl or

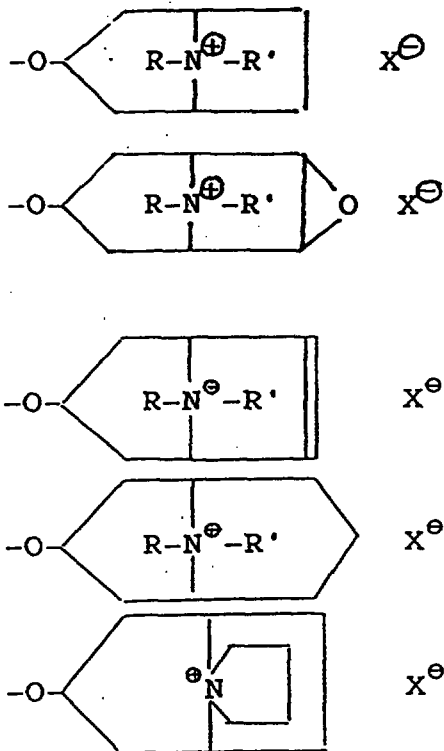
cyclohexyl radical, wherein these radicals may also be methyl-substituted, thienyl and phenyl may also be fluoro-substituted or chloro-substituted,

R_2 represents hydrogen, OH, C_1 - C_4 -alkoxy or C_1 - C_4 -alkyl,

R_a represents H, F, Cl or CH_3 .

In the compounds of formula I, R_1 preferably represents thienyl, R_2 preferably represents OH. The group -OA preferably has the α -configuration and is derived from, for example scopine, tropine, granatoline or 6,7-dehydrotropine or the corresponding nor-compounds; however, -OA may also have the β -configuration, as in pseudotropine, pseudoscopine.

Corresponding radicals are, for example



The substituent R is preferably a lower alkyl radical,

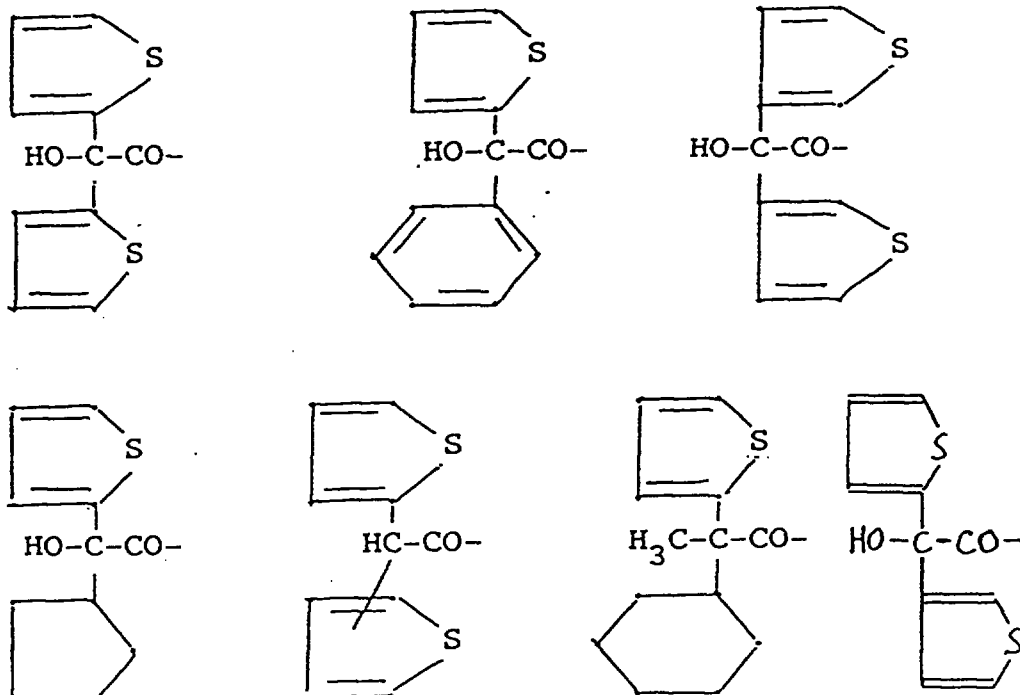
such as CH_3 , C_2H_5 , $n\text{-C}_3\text{H}_7$, $i\text{-C}_3\text{H}_7$, R' is preferably CH_3 . R and R' together are, for example $-(\text{CH}_2)_5-$. As halogen substituents for R , F or, as second choice, Cl are suitable.

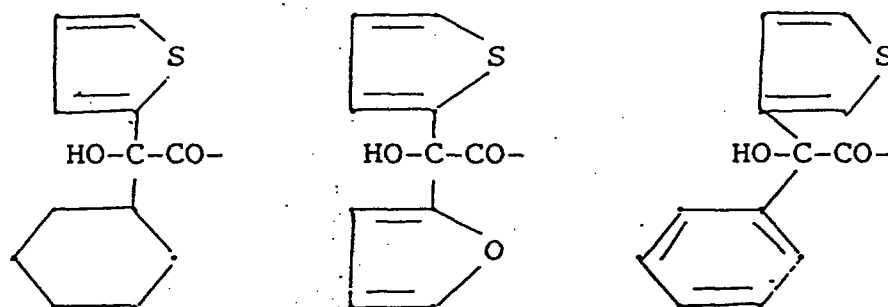
If R denotes a halogen-substituted or hydroxy-substituted alkyl radical, it is preferably $-\text{CH}_2-\text{CH}_2\text{F}$ or $-\text{CH}_2-\text{CH}_2\text{OH}$. Accordingly, the group A represents, for example the radicals of scopine, N -ethylnorscopine, N -isopropyl-norscopine, tropine, N -isopropyl-nortropine, 6,7-dehydrotropine, N - β -fluoroethyl-nortropine, N -isopropyl-6,7-dehydronortropine, N -methylgranatoline as the corresponding quaternary compounds, wherein the anion is preferably Br^- or CH_3SO_3^- .

As the acid radical



the following are particularly suitable:





The compounds of the invention are strong anti-cholinergic agents and have prolonged action. Action lasting at least 24 hours is achieved at inhaled dosages in the μg range. In addition, the toxicity is in the same range as the commercial product Ipratropium bromide, while at the same time the therapeutic effect is stronger.

The novel compounds are suitable, in accordance with their anti-cholinergic nature, for example for the treatment of chronic obstructive bronchitis and (slight to moderately severe) asthma, also for the treatment of vagally induced sinus bradycardia.

Whereas application of the novel active ingredients (in particular the quaternary compounds) by inhalation is mainly recommended for respiratory tract diseases, as a result of which side-effects are largely eliminated, the application for sinus bradycardia is preferably carried out intravenously or orally. It has thus proved to be advantageous that the novel compounds leave the gastro/intestinal motility largely unaffected.

Acta Chem. Scand, Vol. 24 (1970) pp. 1590-6 discloses the preparation of 3-tropanyl-2,2'- or 3,3'-dithienylglycolate. No mention is made of any

physiological properties of these tertiary compounds. The tropine ester of phenyl-2-thienylglycolate is known from J. Chem. Soc. (1957), pp. 3575-8 which also mentions the spasmolytic action of the compound on the isolated intestines of a rabbit. There is no mention of the compound having a surprisingly strong and long-lasting action as a broncholytic agent by converting it into corresponding quaternary compounds.

N-substituted norgranatanol-3 β -ester is disclosed by GB 955 535. According to this document, these compounds are characterised as anti-cholinergic agents which have an excellent central action. The compounds which have a particularly long-lasting broncholytic effect are not disclosed by the British document.

For administration the compounds of the invention are processed using known auxiliaries and/or excipients to give conventional galenic preparations, for example inhalation solutions, suspensions in liquified propellants, preparations containing liposomes or proliposomes, injection solutions, tablets, coated tablets, capsules, inhalation powders for use in conventional inhalation apparatus.

Formulation examples (measures in weight per cent):

1. Controlled dosage aerosol

Active ingredient according to the invention	0.005
Sorbitan trioleate	0.1
Monofluorotrichloromethane and Difluorodichloromethane 2 : 3	
	to 100

The suspension is poured into a conventional aerosol container with a dosage valve. 50 μ l of suspension are preferably dispensed per actuation. The active ingredient may also be metered in a higher amount if required (for example 0.02 wt.%).

2. Tablets

Active ingredient according to the invention	0.05
Colloidal silicic acid	0.95
Lactose	65.00
Potato starch	28.00
Polyvinylpyrrolidone	3.00
Na cellulose glycolate	2.00
Magnesium stearate	1.00

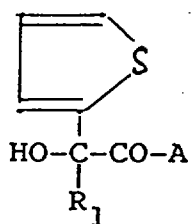
The constituents are processed in conventional manner to give tablets of 200 mg.

The advantageous properties of the novel compounds are shown, for example, in the inhibition of broncholysis in the rabbit (acetylcholine spasms intravenously).

After intravenous administration of the novel active ingredients (dosage 3 $\mu\text{g/kg}$ intravenously), the maximum effect occurred after 10 to 40 minutes. After 5 hours the inhibiting effect had still not been reduced to half, that is to say the half effect time is more, in some cases considerably more, than 5 hours, as made clear by the residual effects after 5 hours listed below:

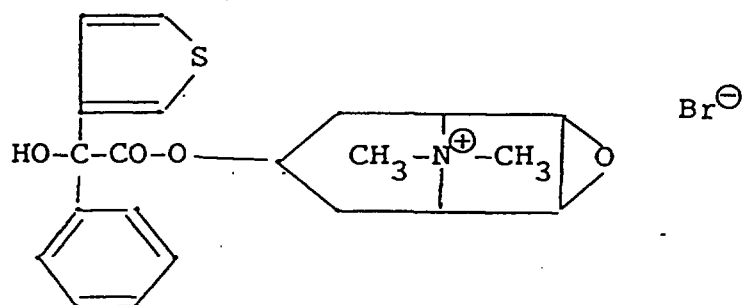
Compound	Residual effect in %
A	76
B	76
C	81
D	61
E	68
F	73
G	69

Compounds of the formula



Compound	A	R ₁
A		2-thienyl
B		3-thienyl
D		2-thienyl
E		3-thienyl
F		cyclopentyl
G		cyclopentyl

Compound C

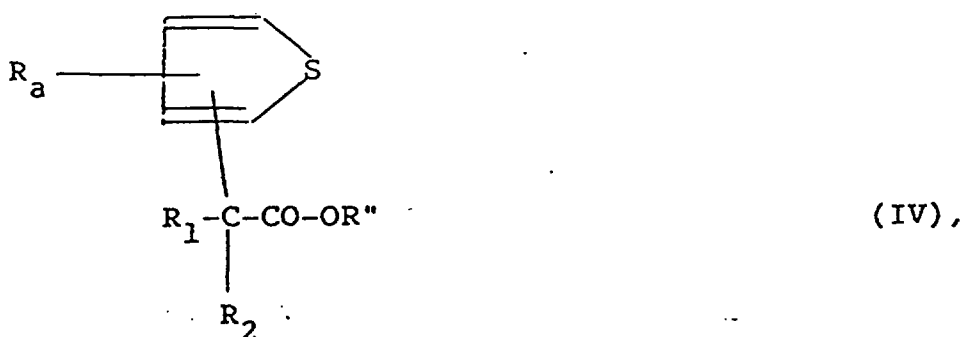


Notes:

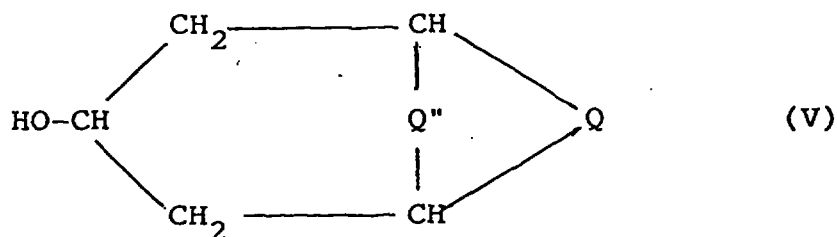
1. The compounds in which R_1 is not 2-thienyl are racemates.
2. The compounds are 3 α -compounds in each case.

Processes known per se are used to prepare the novel compounds.

An ester of the formula



wherein R'' represents a C_1 - C_4 -alkyl radical, preferably a methyl or ethyl radical (R_1 , R_2 and R_a have the above meanings), is preferably transesterified using an amino alcohol of the formula



wherein Q has the above meaning, Q'' represents -NR or -NH and the OH group is in the α - or β -position, in the presence of a conventional transesterification catalyst, and the compound obtained is quaternised

a) if Q'' denotes -NR, using a reactive mono-functionalised derivative Z-(C₁-C₄-alkyl) of a corresponding alkane (Z = leaving group)

or is quaternised

b) if Q'' denotes =NH, using a terminally disubstituted alkane Z-(C₄-C₆-alkylene)-Z without isolation of intermediates.

The transesterification is carried out with heat in an organic solvent, for example toluene, xylene, heptane, or in a melt, strong bases such as sodium methylate, sodium ethylate, sodium hydride, metallic sodium, being used as catalyst. Reduced pressure is used to remove the released lower alcohol from the equilibrium, the alcohol is optionally distilled off azeotropically. The transesterification takes place at temperatures which in general do not exceed 95°C. Transesterification often proceeds more favourably in a melt.

known per se from acid addition salts of the tertiary amines using suitable basic compounds. Quaternisation is carried out in suitable solvents, for example acetonitrile or acetonitrile/methylene chloride, preferably at room temperature; a corresponding alkyl halide, for example alkyl bromide, is preferably used in the process as quaternising agent. Transesterification products wherein Q" represents NH are used as starting materials for those compounds in which R and R' together represent a C₄-C₆-alkylene group. Conversion into the tertiary and then quaternary compound then takes place with the aid of suitable 1,4-dihaloalkanes, 1,5-dihaloalkanes or 1,6-dihaloalkanes without isolation of intermediates.

The starting materials may be obtained analogously to known compounds - in as much as they have not already been described.

Examples:

methyl di-(2-thienyl)glycolate from dimethyl oxalate and 2-thienyl magnesium bromide;

ethyl di-(2-thienyl)glycolate from (2-thienyl)glyoxylic acid and 2-thienyl lithium;

ethyl hydroxy-phenyl-(2-thienyl)acetate from methyl phenylglyoxylate and 2-thienyl magnesium bromide or from methyl (2-thienyl)glyoxylate and phenyl magnesium bromide.

Methyl 2-thienylglyoxylate and cyclohexyl or cyclopentyl magnesium bromide may be reacted in a similar manner.

Several processes are also available for the preparation of the amino alcohols.

Pseudoscopine may be obtained in accordance with M. Polonovski et al., Bull. soc. chim. 43, 79 (1928).

Pseudotropenol may be removed from the mixture

(fractional crystallisation or distillation) which is obtained, for example in accordance with V. Hayakawa et al., J. Amer. Chem. Soc. 1978, 100(6), 1786 or R. Noyori et al., J. Amer. Chem. Soc. 1974, 96(10), 3336.

The corresponding methyl esters may be prepared in a conventional manner starting from 2-furylglyoxynitrile or 3-furylglyoxynitrile via the 2-furylglyoxylic acid or 3-furylglyoxylic acid which can be obtained therefrom. The corresponding glycolates are obtained from these as described using the organometallic derivatives of 2-bromothiophene or 3-bromothiophene. The organometallic compounds which can be obtained from 2-, 3- or 4-halopyridine can be reacted with methyl 2-thienylglyoxylate or methyl 3-thienylglyoxylate to give the corresponding glycolates.

Thienylglycolates, in which the thiophene ring contains fluorine in the 2- or 3-position, are prepared, for example starting from 2-fluorothiophene or 3-fluorothiophene (bromination to give 2-bromo-3-fluorothiophene or 2-bromo-5-fluorothiophene), and after conversion to the corresponding organometallic compounds, reaction with suitable glyoxylates to give the glycolates.

2-Fluorothiophene and 3-fluorothiophene can be reacted analogously to Unterhalt, Arch. Pharm. 322, 839 (1989) to give the corresponding glyoxylates which in turn, as already described, may be reacted with, for example 2-thienyl or 3-thienyl derivatives, to give glycolates. Symmetrically substituted di-thienylglycolates can be prepared analogously by selecting suitable components.

A further route is available via a process analogous to the benzoin condensation and benzilic acid rearrangement.

The following examples illustrate the invention without limiting it.

Example 1

Scopine di-(2-thienyl)glycolate

50.87 g (0.2 mole) of methyl di-(2-thienyl)glycolate and 31.04 g (0.2 mole) of scopine are dissolved in 100 ml of absolute toluene and reacted at a bath temperature of 90°C with addition of 1.65 g (0.071 gram atom) of sodium in several portions. The resulting methanol is distilled off at a reaction mixture temperature of 78 - 90°C under a pressure of 500 mbar. After a reaction time of about 5 hours, the reaction mixture is stirred into a mixture of ice and hydrochloric acid. The acid phase is separated off, rendered alkaline using sodium carbonate and the free base is extracted using methylene chloride. After drying over sodium sulphate, the methylene chloride is distilled off under reduced pressure and the residue is recrystallised from acetonitrile; beige-coloured crystals (from acetonitrile),
m.p. 149 - 50°C,
Yield: 33.79 g (44.7 % of theory).

Example 2

Scopine di-(2-thienyl)glycolate

12.72 g (0.05 mole) of methyl di-(2-thienyl)glycolate and 7.76 g (0.05 mole) of scopine are melted in a heating bath at 70°C under a water jet vacuum. 2.70 g (0.05 mole) of sodium methylate are introduced into this melt and heated for 1 hour in a heating bath at 70°C under a water jet vacuum and subsequently for a further hour in a heating bath at 90°C. The solidified melt is

taken up in a mixture of 100 ml of water and 100 ml of methylene chloride while monitoring the temperature, and the methylene chloride phase is extracted several times using water. The methylene chloride phase is extracted using the corresponding amount of dilute hydrochloric acid. The scopine di-(2-thienyl)glycolate is extracted from the combined aqueous phases using methylene chloride after adding the corresponding amount of sodium carbonate and dried over sodium sulphate. The hydrochloride is prepared from the dried methylene chloride solution in a conventional manner. The crystals are filtered off under suction, washed using acetone and dried under reduced pressure at 35°C. Pale yellow crystals (from methanol), m.p. 238 - 41°C (decomposition);

Yield: 10.99 g (53.1 % of theory).

The hydrochloride may be converted to the base in a conventional manner.

Example 3

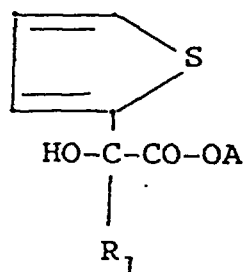
Scopine di-(2-thienyl)glycolate

38.15 g (0.15 mole) of methyl di-(2-thienyl)glycolate and 23.28 g (0.15 mole) of scopine are mixed, 0.34 g (0.015 gram atom) of sodium is added and the mixture is melted in a heating bath at 90°C under a water jet vacuum. The reaction lasts 2.5 hours. 100 ml of absolute toluene are then added and the mixture is stirred at a heating bath temperature of 90°C until a solution is produced. The reaction solution is cooled to room temperature and stirred into a mixture of ice and hydrochloric acid cooled using ice. The hydrochloride of the basic ester crystallising out is filtered off under suction and washed using a small amount of water and a large amount of diethyl ether. The filtrate phases are separated off and the aqueous

phase is extracted using diethyl ether. The hydrochloride filtered off under suction is suspended in the (acid) aqueous phase and converted to the base while monitoring the temperature and adding the corresponding amount of sodium carbonate; the base is extracted using methylene chloride. The combined methylene chloride phases are dried over sodium sulphate. After distilling off the methylene chloride, crystals remain which are purified over active charcoal and recrystallised from acetonitrile. Pale yellow crystals (from acetonitrile), m.p. 148 - 49°C; Yield: 39.71 g (70.1 % of theory).

Table I

Compounds of the formula



No.	A	R_1	M.p. [°C]	
			Base	Hydro-chloride
1	3 α -(6 β ,7 β -epoxy)-tropanyl	2-thienyl	149-50	238-41
2	3 α -tropanyl	2-thienyl	167-8	253
3	3 α -(6,7-dehydro)-tropanyl	2-thienyl	164-5	
4	3 α -(N- β -fluoroethyl)- nortropanyl	2-thienyl		236
5	3 α -(N-isopropyl)- granatanyl	2-thienyl		232
6	3 α -(N-isopropyl)- nortropanyl	2-thienyl		256
7	3 α -(6 β ,7 β -epoxy)-N- isopropyl-nortropanyl	2-thienyl		206
8	3 α -(6 β ,7 β -epoxy)-N-ethyl- nortropanyl	2-thienyl		212-3
9	3 α -(N-ethyl)-nortropanyl	2-thienyl		256-7
10	3 α -(N-N-methyl)-granatanyl	2-thienyl		241
11	3 α -(6 β ,7 β -epoxy)-N- β - fluoroethylnortropanyl	2-thienyl		188-90

No.	A	R ₁	Base	M.p. [°C] Hydro- chloride
12	3α-(6β,7β-epoxy)-N-n-propylnortropanyl	2-thienyl		104-6
13	3α-(6β,7β-epoxy)-N-n-butylnortropanyl	2-thienyl		225-7
14	3α-(6β,7β-epoxy)-tropanyl	phenyl		246-7
15	3α-tropanyl	phenyl		243-4
16	3α-(N-β-fluoroethyl)-nortropanyl	phenyl		219-20
17	3α-(6,7-dehydro)-tropanyl	phenyl		181-3
18	3α-(N-ethyl)-nortropanyl	phenyl		231-2
19	3α-(N-isopropyl)-nortropanyl	phenyl		246-7
20	3α-tropanyl	cyclohexyl		260
21	3α-(N-β-fluoroethyl)-nortropanyl	cyclohexyl		203-4
22	3α-(6β,7β-epoxy)-tropanyl	cyclopentyl		237
23	3α-tropanyl	cyclopentyl		260
24	3α-(N-β-fluoroethyl)-nortropanyl	cyclopentyl		182-3
25	3α-(N-ethyl)-nortropanyl	cyclopentyl		227-8
26	3α-(N-isopropyl)-nortropanyl	cyclopentyl		174-5
27	3β-(6β,7β-epoxy)-tropanyl	2-thienyl		240-2
28	3β-tropanyl	2-thienyl		217-9
29	3β-(6,7-dehydro)-tropanyl	2-thienyl		233-5
30	3α-(6,7-dehydro)-tropanyl	3-thienyl		247-8
31	3α-(6β,7β-epoxy)-tropanyl	3-thienyl		242-3
32	3α-(6β,7β-epoxy)-tropanyl	2-furyl		
33	3α-(6,7-dehydro)-tropanyl	2-furyl		
34	3α-tropanyl	2-furyl		
35	3α-tropanyl	2-pyridyl		
36	3α-(6β,7β-epoxy)-tropanyl	2-pyridyl		

No.	A	R ₁	Base	M.p. [°C] Hydro- chloride
12	3α-(6β,7β-epoxy)-N-n-propylnortropanyl	2-thienyl		104-6
13	3α-(6β,7β-epoxy)-N-n-butylnortropanyl	2-thienyl		225-7
14	3α-(6β,7β-epoxy)-tropanyl	phenyl		246-7
15	3α-tropanyl	phenyl		243-4
16	3α-(N-β-fluoroethyl)-nortropanyl	phenyl		219-20
17	3α-(6,7-dehydro)-tropanyl	phenyl		181-3
18	3α-(N-ethyl)-nortropanyl	phenyl		231-2
19	3α-(N-isopropyl)-nortropanyl	phenyl		246-7
20	3α-tropanyl	cyclohexyl		260
21	3α-(N-β-fluoroethyl)-nortropanyl	cyclohexyl		203-4
22	3α-(6β,7β-epoxy)-tropanyl	cyclopentyl		237
23	3α-tropanyl	cyclopentyl		260
24	3α-(N-β-fluoroethyl)-nortropanyl	cyclopentyl		182-3
25	3α-(N-ethyl)-nortropanyl	cyclopentyl		227-8
26	3α-(N-isopropyl)-nortropanyl	cyclopentyl		174-5
27	3β-(6β,7β-epoxy)-tropanyl	2-thienyl		240-2
28	3β-tropanyl	2-thienyl		217-9
29	3β-(6,7-dehydro)-tropanyl	2-thienyl		233-5
30	3α-(6,7-dehydro)-tropanyl	3-thienyl		247-8
31	3α-(6β,7β-epoxy)-tropanyl	3-thienyl		242-3
32	3α-(6β,7β-epoxy)-tropanyl	2-furyl		
33	3α-(6,7-dehydro)-tropanyl	2-furyl		
34	3α-tropanyl	2-furyl		
35	3α-tropanyl	2-pyridyl		
36	3α-(6β,7β-epoxy)-tropanyl	2-pyridyl		

No.	A	R ₁	Base	M.p. [°C] Hydro- chloride
37	3 α -(6,7-dehydro)-tropanyl	2-pyridyl		
38	3 α -tropanyl	3-thienyl		
39	3 α -(6,7-dehydro)-tropanyl	cyclopentyl		
40	3 α -(6 β ,7 β -epoxy)-tropanyl	cyclohexyl		
41	3 α -(6,7-dehydro)-tropanyl	cyclohexyl		

Note: All hydrochlorides melt with decomposition.

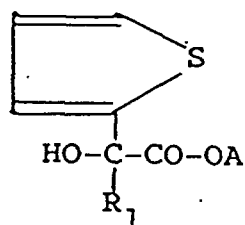
Example 4

Scopine di-(2-thienyl)glycolate methobromide

10.0 g (0.0265 mole) of scopine di-(2-thienyl)glycolate are dissolved in a mixture comprising 20 ml of anhydrous methylene chloride and 30 ml of anhydrous acetonitrile and treated with 12.8 g (0.1325 mole) of methyl bromide (as 50 % strength solution in anhydrous acetonitrile), and the reaction mixture is allowed to stand for 24 hours at room temperature in a tightly sealed reaction vessel. Crystals are precipitated during this time. They are filtered off under suction, washed using methylene chloride and dried at 35°C under reduced pressure. White crystals (from methanol/acetone), m.p. 217 - 8°C (decomposition) after drying at 111°C under reduced pressure.

Table II

Quaternary compounds of the formula



No.	A	R ₁	M.p. [°C]
1	3α-(6β,7β-epoxy)-tropanyl methobromide	2-thienyl	217-18
2	3α-tropanyl methobromide	2-thienyl	263-64
3	3α-(6,7-dehydro)-tropanyl methobromide	2-thienyl	191-92
4	3α-(N-β-fluoroethyl)- nortropanylmethobromide	2-thienyl	242-43
5	3α-tropanyl-β- fluoroethobromide	2-thienyl	214-15
6	3α-(N-isopropyl)- granatanyl methobromide	2-thienyl	229-30
7	3α-(N-isopropyl)- nortropanylmethobromide	2-thienyl	245-46
8	3α-(6β,7β-epoxy)-N- isopropyl-nortropanyl methobromide	2-thienyl	223-24
9	3α-(6β,7β-epoxy)-N- ethylnortropanyl methobromide	2-thienyl	215-16
10	3α-(N-ethyl)-nortropanyl methobromide	2-thienyl	260-61

No.	A	R ₁	M.p. [°C]
11	3 α -(N-methyl)-granatanyl-methobromide	2-thienyl	246-47
12	3 α -(6 β ,7 β -epoxy)-N-fluoroethyl-nortropanyl methobromide	2-thienyl	182-83
13	3 α -(6 β ,7 β -epoxy)-N-n-propylnortropanyl methobromide	2-thienyl	209-10
14	3 α -tropanyl- β -hydroxyethobromide	2-thienyl	231-32
15	3 α -(6,7-epoxy)-tropanyl methobromide	phenyl	217-18
16	3 α -tropanyl methobromide	phenyl	273-74
17	3 α -(N- β -fluoroethyl)-nortropanylmethobromide	phenyl	215
18	3 α -(6,7-dehydro)-tropanyl methobromide	phenyl	170-71
19	3 α -(N-ethyl)-nortropanyl methobromide	phenyl	249-50
20	3 α -(N-isopropyl)-nortropanyl methobromide	phenyl	259-60
21	3 α -tropanyl ethobromide	phenyl	248-49
22	3 α -(N-ethyl)-nortropanyl ethobromide	phenyl	244-45
23	3 α -(6,7-epoxy)-tropanyl ethobromide	phenyl	226
24	3 α -tropanyl- β -fluoroethobromide	phenyl	241
25	3 α -tropanyl methobromide	cyclohexyl	278
26	3 α -(N-fluoroethyl)-nortropanyl methobromide	cyclohexyl	198
27	3 α -tropanyl- β -fluoroethobromide	cyclohexyl	233-34

No.	A	R ₁	M.p. [°C]
28	3 α -tropanyl methobromide	cyclopentyl	260
29	3 α -tropanyl ethobromide	cyclopentyl	235-36
30	3 α -(N-ethyl)-nortropanyl methobromide	cyclopentyl	251-52
31	3 α -(N-isopropyl)- nortropanyl-methobromide	cyclopentyl	244-45
32	3 α -tropanyl- β - fluoroethobromide	cyclopentyl	189-90
33	3 α -(N- β -fluoroethyl)- nortropanyl-methobromide	cyclopentyl	226-27
34	3 α -(6,7-dehydro)-tropanyl metho-methanesulphonate	2-thienyl	225-6
35	3 β -(6 β ,7 β -epoxy)-tropanyl methobromide	2-thienyl	218-20
36	3 β -tropanyl methobromide	2-thienyl	243-4
37	3 β -(6,7-dehydro)-tropanyl methobromide	2-thienyl	211-4
38	3 α -(6,7-dehydro)-tropanyl methobromide	3-thienyl	182-3*
39	3 α -(6 β ,7 β -epoxy)-tropanyl methobromide	3-thienyl	217-8
40	(+) enantiomer of No. 1		
41	(-) enantiomer of No. 1		
42	3 α -(6 β ,7 β -epoxy)-tropanyl methobromide	2-furyl	
43	3 α -(6,7-dehydro)-tropanyl methobromide	2-furyl	
44	3 α -tropanyl methobromide	2-furyl	
45	3 α -(6 β ,7 β -epoxy)-tropanyl methobromide	2-pyridyl	
46	3 α -(6,7-dehydro)-tropanyl methobromide	2-pyridyl	
47	3 α -tropanyl methobromide	2-pyridyl	
48	3 α -tropanyl methobromide	3-thienyl	

No.	A	R ₁	M.p. [°C]
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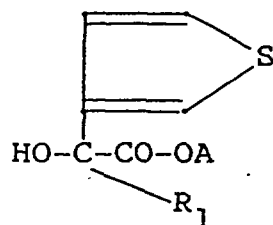
49	3 α -(6,7-dehydro)-tropanyl methobromide	cyclopentyl	
50	3 α -(6 β ,7 β -epoxy)-tropanyl methobromide	cyclohexyl	
51	3 α -(6,7-dehydro)-tropanyl methobromide	cyclohexyl	
52	3 α -(6 β ,7 β -epoxy)-tropanyl methobromide	cyclopentyl	

* contains crystalline methanol

Note: All compounds in the table melt with decomposition.

Table III

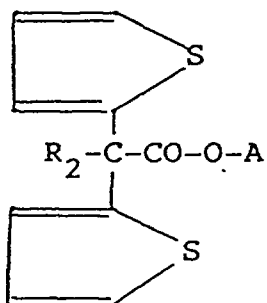
Compounds of the formula



No.	A	R_1	M.p. [°C]
			Hydrochloride
1	3 α -(6 β ,7 β -epoxy)-tropanyl	phenyl	246-7
2	3 α -(6,7-dehydro)-tropanyl	phenyl	261-2
3	3 α -(6 β ,7 β -epoxy)-tropanyl	3-thienyl	
4	3 α -(6,7-dehydro)-tropanyl	3-thienyl	
5	3 α -tropanyl	3-thienyl	
6	3 α -(N-methyl)-granatanyl	3-thienyl	

Table IV

Compounds of the formula

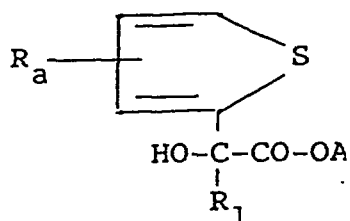


No.	A	R ₂	M.p. [°C] Hydrochloride

1	3α-(6β,7β-epoxy)-tropanyl	H	
2	3α-(6,7-dehydro)-tropanyl	H	
3	3α-(6β,7β-epoxy)-tropanyl	methyl	
4	3α-(6,7-dehydro)-tropanyl	methyl	210-2.5
5	3α-(6β,7β-epoxy)-tropanyl	methoxy	
6	3α-(6,7-dehydro)-tropanyl	methoxy	

Table V

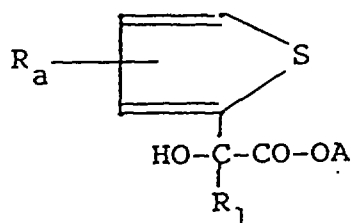
Compounds of the formula



No.	A	R ₁	R _a	M.p. [°C]
1	3α-(6β,7β-epoxy)-tropanyl	2-thienyl	5-methyl	
2	3α-(6,7-dehydro)-tropanyl	2-thienyl	5-methyl	
3	3α-tropanyl	2-thienyl	5-methyl	
4	3α-(6α,7β-epoxy)-tropanyl	2-(5-methyl)- thienyl	5-methyl	
5	3α-(6,7-dehydro)-tropanyl	2-(5-methyl)- thienyl	5-methyl	
6	3α-tropanyl	2-(5-methyl)- thienyl	5-methyl	
7	3α-(6β,7β-epoxy)-tropanyl	2-thienyl	5-fluoro	
8	3α-(6,7-dehydro)-tropanyl	2-thienyl	5-fluoro	
9	3α-tropanyl	2-thienyl	5-fluoro	
10	3α-(6β,7β-epoxy)-tropanyl	2-(5-fluoro)- thienyl	5-fluoro	
11	3α-(6,7-dehydro)-tropanyl	2-(5-fluoro)- thienyl	5-fluoro	
12	3α-tropanyl	2-(5-fluoro)- thienyl	5-fluoro	

Table VI

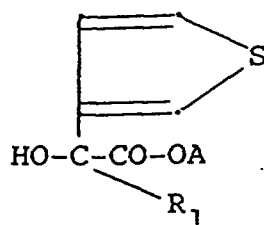
Compounds of the formula



No.	A	R ₁	R _a M.p. [°C]
1	3α-(6β,7β-epoxy)-tropanyl methobromide	2-thienyl	5-methyl
2	3α-(6,7-dehydro)-tropanyl methobromide	2-thienyl	5-methyl
3	3α-tropanyl-methobromide	2-thienyl	5-methyl
4	3α-(6β,7β-epoxy)-tropanyl methobromide	2-(5-methyl)-thienyl	5-methyl
5	3α-(6,7-dehydro)-tropanyl methobromide	2-(5-methyl)-thienyl	5-methyl
6	3α-tropanyl methobromide	2-(5-methyl)-thienyl	5-methyl
7	3α-(6β,7β-epoxy)-tropanyl methobromide	2-thienyl	5-fluoro
8	3α-(6,7-dehydro)-tropanyl methobromide	2-thienyl	5-fluoro
9	3α-tropanyl methobromide	2-thienyl	5-fluoro
10	3α-(6β,7β-epoxy)-tropanyl methobromide	2-(5-fluoro)-thienyl	5-fluoro
11	3α-(6,7-dehydro)-tropanyl methobromide	2-(5-fluoro)-thienyl	5-fluoro
12	3α-tropanyl methobromide	2-(5-fluoro)-thienyl	5-fluoro

Table VII

Compounds of the formula

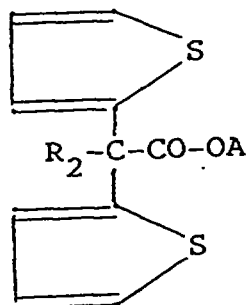


No.	A	R ₁	M.p. [°C]
1	3α-(6β,7β-epoxy)-tropanyl methobromide	phenyl	211-2
2	3α-(6,7-dehydro)-tropanyl methobromide	phenyl	158-60*
3	3α-(6β,7β-epoxy)-tropanyl methobromide	3-thienyl	
4	3α-(6,7-dehydro)-tropanyl methobromide	3-thienyl	
5	3α-tropanyl methobromide	3-thienyl	
6	3α-(N-methyl)-granatanyl methobromide	3-thienyl	

* (with crystalline methanol)

Table VIII

Quaternary compounds of the formula



No.	A	R ₂	M.p. [°C]
1	3α-(6β,7β-epoxy)-tropanyl methobromide	H	
2	3α-(6,7-dehydro)-tropanyl methobromide	H	
3	3α-(6β,7β-epoxy)-tropanyl methobromide	methyl	
4	3α-(6,7-dehydro)-tropanyl methobromide	methyl	206-8
5	3α-tropanyl methobromide	methoxy	
6	3α-(N-methyl)-tropanyl methobromide	methoxy	

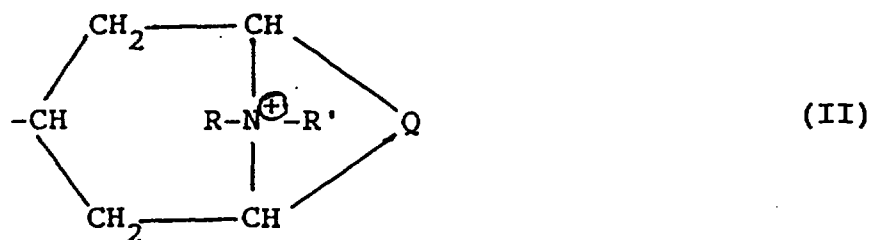
Claims

1. Compounds of formula



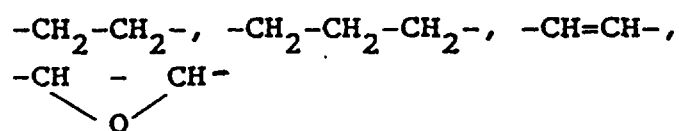
in which

A represents the group



wherein

Q represents one of the double-bonding groups



and



R denotes an optionally halogen-substituted or hydroxy-substituted C_1-C_4 alkyl radical, R' denotes a C_1-C_4 alkyl radical and R and R' together may also form a C_4-C_6 alkylene radical and one equivalent of an anion ($X^\ominus$) opposes the positive charge of the N-atom,

R_1 represents a thienyl, phenyl, furyl, cyclopentyl or cyclohexyl radical, whereby these radicals may also be methyl-substituted, thienyl and phenyl may also be fluoro-substituted or chloro-substituted,

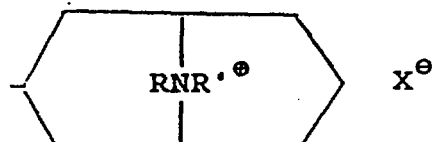
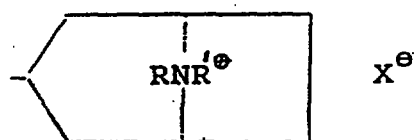
R_2 represents hydrogen, OH, C_1-C_4 -alkoxy or C_1-C_4 alkyl,

R_3 represents H, F, Cl or CH_3 .

2. Compounds according to claim 1, wherein R_1 represents 2-thienyl.

3. Compounds according to either claim 1 or 2, wherein R_2 represents OH.

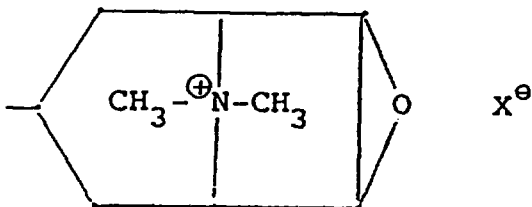
4. Compounds according to claim 1, 2 or 3, wherein A represents



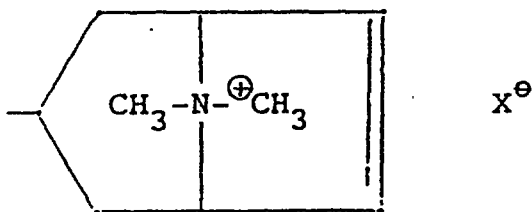
R

and $X^\ominus$ have the above meaning and R' has the above meaning with the exclusion of hydrogen.

5. Compounds according to claims 1 to 4, in which R_1 denotes 2-thienyl and A represents the group

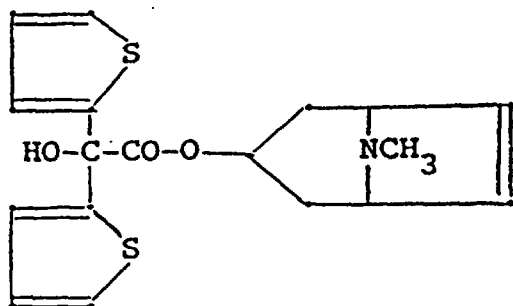
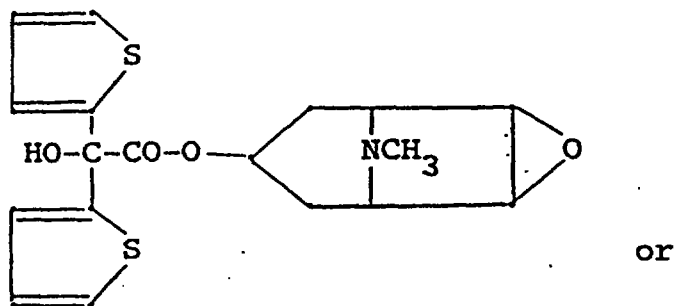


or



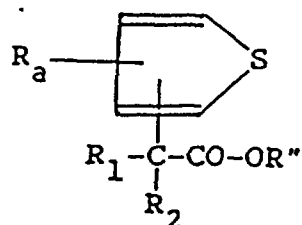
in the 3 α -form, wherein $X^\ominus$ is one equivalent of an anion, preferably $Br^\ominus$ or $CH_3SO_3^\ominus$.

6. Compounds of Formula



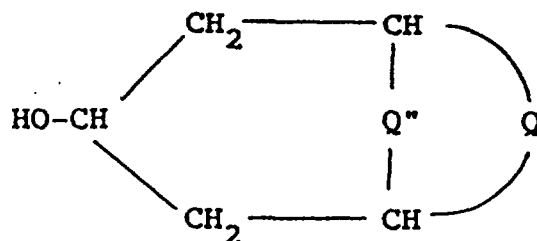
in the 3 α -form as methobromides or methomethane-sulfonates.

7. Medicaments characterised by an amount of a compound according to claims 1 to 6 in addition to conventional auxiliaries and/or excipients.
8. Use of compounds according to claims 1 to 6 for preparing anticholinergic medicaments.
9. Use of compounds according to claims 1 to 6 for preparing medicaments for the treatment of respiratory tract diseases and sinus bradycardia.
10. A process for preparing the compounds according to claims 1 to 6, characterised in that an ester of Formula



(IV)

wherein R'' represents a C₁-C₄ alkyl radical and R₁, R₂ and R_a have the above meaning is transesterified using an amino alcohol of Formula

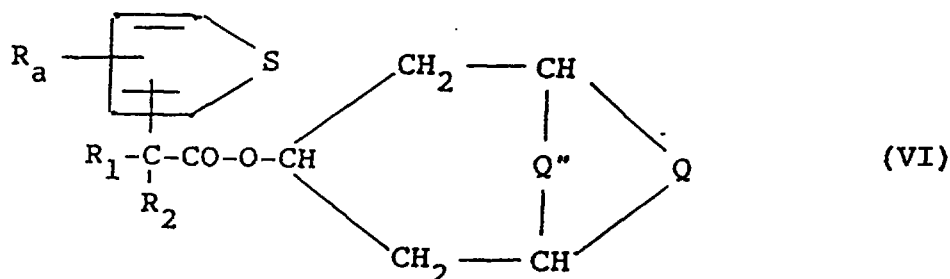


(V)



wherein

Q has the above meaning and Q" represents =NR or =NH, in an inert organic solvent or in the melt, in the presence of a transesterification catalyst, and the resultant compound of Formula



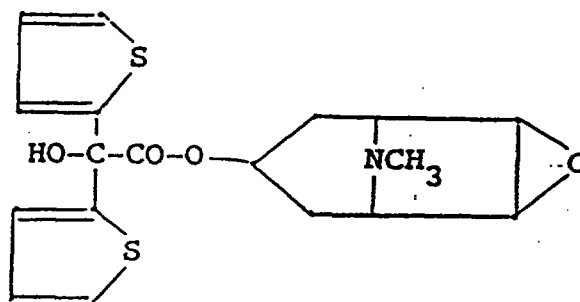
- a) is quaternised using a reactive monoderivative Z-(C₁-C₄-alkyl) of an alkane (Z=leaving group), if Q" denotes =NR

or

- b) is substituted and quaternised using a terminally disubstituted alkane Z-(C₄-C₆-alkylene)-Z without intermediate isolation, if Q" denotes =NH.

11. Compounds of Formula VI, in which Q, Q", R_a, R₁ and R₂ have the above meaning, and their acid additions salts thereof with the proviso that the tropine esters of phenyl-2-thienylglycolic acid, 2,2'-dithienylglycolic acid and 3,3'-dithienylglycolic acid are excluded.

12. Compounds according to Claim 11, wherein Formula VI represents



or

