Analysis of Confiscated Black Market Drugs Using Chromatographic and Mass Spectrometric Approaches

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Abstract

In the context of house searches in Germany, numerous drugs were confiscated and subjected to chemical analysis, including anabolic agents such as various anabolic-androgenic steroids (stanozolol, testosterone derivatives, trenbolone esters, etc.) and clenbuterol, as well as agents with anti-estrogenic activity (tamoxifen, clomiphene), drugs stimulating virility (sildenafil, tadalafil), and unlabeled plastic bags. Liquid chromatography–tandem mass spectrometry, gas chromatography–mass spectrometry with nitrogen-phosphorus specific detection, gel electrophoresis, and immunological tests were employed to test for the effective content of 70 products. In 18 cases (25.7%), the declared ingredients differed from the actual content, in particular concerning anabolic-androgenic steroids. Nandrolone and trenbolone esters, for instance, were frequently substituted or complemented by various testosterone derivatives, and several testosterone depot formulations originally composed of four different esters were found to contain fewer or wrong components. Except for those drugs supposedly originating from so-called underground labs, fake packings were hardly or not distinguishable from original boxes by visual inspection.

Introduction

The issue of black market drugs, regarding anabolic steroids and other agents relevant for doping controls in particular, was recognized several decades ago. The aim to increase physical performance but also to improve appearance and body shape has been mentioned frequently as a major reason for drug use and abuse by people participating in anonymous surveys. However, great concerns have arisen regarding health issues related to the uncontrolled use of compounds and the commonly negligible knowledge about side effects associated, for instance, with applications of supraphysiological doses of steroid hormones. According to so-called underground literature (1), therapeutic dosages are exceeded several-fold (up to tenfold) when following the described recommendations, and resulting side effects such as the reduction in vessel-protective HDL cholesterol, early atherosclerosis, prothrombotic effects, liver tumors, and others were observed in numerous case studies with and without lethal consequences (2–11).

During the last 10 years, numerous products that supposedly support athletic performance and muscle growth were obtained from different commercial sources (e.g., via Internet order) but also confiscated in house searches. Several of those were identified as counterfeit substances. In the present report, we describe the analysis of 70 products collected from three different individuals under suspicion for dealing with prescription drugs and illegal compounds. As packaging and labels were not differentiable from original counterparts, aliquots of all drugs were subjected to liquid chromatography–tandem mass spectrometry (LC–MS–MS) or gas chromatography–mass spectrometry with nitrogen-phosphorus specific detection (GC–MS–NPD) in order to determine whether these drugs were authentic or fake products. In addition, unlabeled plastic bags were analyzed for their content using MS approaches with and without chemical derivatization.

Materials and Methods

Confiscated drugs and compounds investigated in the present study are listed in Table I, sorted by findings in the houses of different individuals. Twenty-five different anabolic steroid preparations were found. Nine were labeled as testosterone-based drugs (Testabol Propionate, Testabol Depot, Testovis, Testex Prolongatum, Sustanon, Cidoteston, Testoviron Depot, Testosteron-Depot, and Testofort Injection); four as trenbolone-containing substances (Trenabol, Trenabol Depot, Tri-Trenabol 150, and Trenabol 200); three as metandienone (Anabol Tablets, Danabol DS, and Naposim); two as stanozolol (Winstrol Depot and Stanabol 50); two as nandrolone derivatives (Decabol 250 and Nandrolone Decanoate); and one each of drugs containing metenolone (Primobol 100), boldenone (Boldabol 200), fluoxymesterone (Fluoxymesterone), oxymetholone (Oxythone-50), and mesterolone (Proviron). In

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Table I. Details of Drugs Confiscated in House Searches in Germany

Item	Drug	Active Compound(s)	Formulation	Content/ Unit	Manufacturer	Determined Content
Suspect 1						
1	KAMAGRA 100 mg	Sildenafil (citrate)	"Oral Jelly"	100 mg Sildenafil/bag	India: ajanta pharma, Mumbai (Bombay)	as labeled
2						as labeled
3	Sustanon '250'	T-propionate, T-phenylpropionate, T-isocaproate, T-decanoate	oily solution for i.m. application	1 mL contains: 30 mg T-propionate, 60 mg T-phenylpropionate, 60 mg T-isocaproate, 100 mg T-decanoate	Pakistan: Organon Pakistan, Kerachi	as labeled
4	Viagra	Sildenafil (citrate)	tablet	100 mg Sildenafil/tablet	USA: Pfizer Labs, NY	as labeled
5	Viagra	Sildenafil (citrate)	tablet	100 mg Sildenafil/tablet	Israel: Pfizer Pharmaceuticals Israel Ltd., Herzeliya Pituach	as labeled
6	OXYTONE-50	Oxymetholone	tablet	50 mg/tablet	Thailand: SB Laboratories Onnuj	as labeled
7						as labeled
8	Anabol Tablets	Metandienone	tablet	5 mg/tablet	Thailand: The British Dispensary (L.P.) CO., Ltd. Samutprakarn	Methyltestosterone
9						as labeled
10	Testofort Injection	T-enantate	oily solution for i.m. application	250 mg/ampoule	Pakistan: Pliva Pakistan Ltd, Balochistan	as labeled
11	NANDROLONE DECANOATE NORMA	Nandrolone-Decanoate	oily solution for i.m. application	200 mg/vial	Greece: NORMA HELLAS S.A., Pharmaceutical Industry, Athens	T-enantate
12	Testosteron-Depot 250 mg Eifelfango	T-enantate	oily solution for i.m. application	250 mg/ampoule	Germany: Eifelfango, Bad-Neuenahr-Ahrweiler	as labeled
13						as labeled
14	TESTOVIS	T-propionate	oily solution for i.m. application	100 mg/ampoule	Italy: SIT Specialita Igenica Terapeutiche, Mede	as labeled
15	YOHIMBIN-HCL USP XXIV	Yohimbine-HCl	tablet	10 mg/tablet	International Pharmaceuticals ("Underground Lab")	as labeled
16	Coffeinum N 0.2 g	caffeine	tablets	200 mg/tablet	Germany: Merck dura GmbH, Darmstadt	as labeled
17						as labeled
18	Testoviron Depot	T-enantate	oily solution for i.m. application	250 mg/ampoule	Pakistan: Medipharm Laboratories	as labeled
19	NANDROLONE DECANOATE *NORMA*	Nandrolone-decanoate	oily solution for i.m. application	200 mg/Vial	Greece: NORMA HELLAS S.A., Pharmaceutical Industry, Athens	T-enantate
Suspect 2						
20	NANDROLONE DECANOATE *NORMA*	Nandrolone-decanoate	oily solution for i.m. application	200 mg/vial	Greece: NORMA HELLAS S.A., Pharmaceutical Industry, Athens	T-enantate, T-cypionate
21	Sustanon '250'	T-propionate, T-phenylpropionate T-isocaproate, T-decanoate	oily solution for i.m. application	1 mL contains: 30 mg T-propionate, 60 mg T-phenylpropionate, 60 mg T-isocaproate, 100 mg T-decanoate	Egypt: The NILE Co. for Pharmaceuticals, Cairo	T-propionate, T-phenylpropionate T-cypionate
22	Testoviron Depot	T-enantate	oily solution for i.m. application	250 mg/ampoule	Pakistan: Medipharm Laboratories	as labeled

Continued

Table I. Details of Drugs Confiscated in House Searches in Germany *(Continued)*

Item	Drug	Active Compound(s)	Formulation	Content/ Unit	Manufacturer	Determined Content
23	Tamoxifen AL 30	Tamoxifen	tablets	30 mg/tablet	Germany: Aliud	as labeled
24	YOHIMBIN-HCL USP XXIV	Yohimbine-HCl	tablet	10 mg/tablet	International Pharmaceuticals	as labeled
25	TESTOVIS	T-propionate	oily solution for i.m. application	100 mg/ampoule	Italy: SIT Specialita Igenica Terapeutiche, Mede	as labeled
26 / 27	two bags with unidentified colorless powder					GABA (gamma-aminobutyric acid)
28	Anabol Tablets	Methandienone	tablet	5 mg/tablet	Thailand: The British Dispensary (L.P.) CO., Ltd. Samutprakarn	as labeled
Suspect 3						
29	Cialis 20 mg	Tadalafil	tablet	20 mg/tablet	Lilly	Sildenafil
30	Cidoteston	T-enantate	oily solution for i.m. application	250 mg/ampoule	Egypt: CID Co. Chemical Industries Development, Giza	T-enantate
31						as labeled
32	Clomiphene citrate	Clomiphene-citrate	tablet	50 mg/tablet	Greece: Anfarm Hellas S.A.	as labeled
33	DANABOL DS	Metandienone (Methandrostenolone)	tablet	10 mg/tablet	Thailand: March Pharmaceuticals, Wangthonglang (producer); Body Research, Thonburi (distributor)	as labeled
34						as labeled
35	Fluoxymesterone	Fluoxymesterone	tablet	5 mg/tablet	International Pharma	as labeled
36	KAMAGRA	Sildenafil (citrate)	tablet	100 mg Sildenafil/tablet	India: ajanta pharma, Mumbai (Bombay)	as labeled
37	KAMAGRA	Sildenafil (citrate)	"Oral Jelly"	100 mg Sildenafil/bag	India: ajanta pharma	as labeled
38	NANDROLONE DECANOATE NORMA	Nandrolone-decanoate	oily solution for i.m. application	200 mg/vial	Greece: NORMA HELLAS S.A., Pharmaceutical Industry, Athens	T-enantate
39	Naposim 5 mg	Metandienone	tablet	5 mg/tablet	Terapia	methyltestosterone
40	OXYTONE-50	Oxymetholone	tablet	50 mg/tablet	Thailand: SB Laborat	as labeled
41	Proviron 25 mg	Mesterolone	tablet	25 mg/tablet	Spain: Schering Espana, Madrid	as labeled
42	Sustanon "250"	T-propionate, T-phenylpropionate, T-isocaproate, T-decanoate	oily solution for i.m. application	1 mL contains: 30 mg T-propionate, 60 mg T-phenylpropionate 60 mg T-isocaproate, 100 mg T-decanoate	Egypt: The NILE Co. for Pharmaceuticals, Cairo	T-propionate, T-phenylpropionate T-cypionat
43	Sustanon "250"	T-propionate,	oily solution	1 mL contains:	Pakistan: Organon	as labeled
44		T-phenylpropionate,	for i.m.	30 mg T-propionate,	Pakistan, Kerachi	as labeled
45		T-isocaproate,	application	60 mg T-phenylpropionate		as labeled
46		T-decanoate		60 mg T-isocaproate,		as labeled
47				100 mg T-decanoate		as labeled
48						as labeled
49	Tamoxifen 40	Tamoxifen (citrate)	tablet	40 mg/tablet	Germany: Heumann	as labeled
50					Pharma, Nürnbert	as labeled
51	Testex Prolongatum 250 mg	T-cypionate	oily solution for i.m. application	250 mg/Ampulle	Spain: Q pharma, Alicante	as labeled

Continued

Table I. Details of Drugs Confiscated in House Searches in Germany *(Continued)*

Item	Drug	Active Compound(s)	Formulation	Content/ Unit	Manufacturer	Determined Content
52	TESTOVIS	T-propionate	oily solution for i.m. application	100 mg/ampoule	Italy: SIT Specialita Igenica Terapeutiche, Mede	as labeled
53						as labeled
54						as labeled
55	Thybon 100	Liothyronin-HCl	tablet	100 µg/tablet	Germany: Henning Berlin Arzneimittel GmbH	as labeled
56	Viagra	Sildenafil (citrate)	tablet	100 mg/tablet	Israel: Pfizer Pharmaceuticals Israel Ltd., Herzeliya Pituach	as labeled
57	Winstrol Depot	Stanozolol	suspension for i.m. application	50 mg/ampoule	Spain: Zambon S.A., Barcelona	as labeled
58						as labeled
59						as labeled
60	YOHIMBIN-HCL USP XXIV	Yohimbine-HCl	tablet	10 mg/tablet	International Pharmaceuticals ("Underground Lab")	as labeled
61	Boldabol 200	Boldenone-undecylenate	oily solution for i.m. application	200 mg/mL	British Dragon Pharmaceuticals ("Underground Lab")	as labeled
62	Decabol 250	Nandrolone-decanoate	oily solution for i.m. application	250 mg/mL	British Dragon Pharmaceuticals ("Underground Lab")	Nandrolone-decanoate, T-propionate
63	Primobol 100	Metenolone-enantate	oily solution for i.m. application	100 mg/mL	British Dragon Pharmaceuticals ("Underground Lab")	Nandrolone-decanoate, Nandrolone-phenylpropionate T-propionate, T-phenylpropionate T-enantate
64	Stanabol 50	Stanozolol	white (aqueous) solution for i.m. application	50 mg/mL	British Dragon Pharmaceuticals ("Underground Lab")	as labeled
65	Testabol Depot	T-cypionate	oily solution for i.m. application	200 mg/mL	British Dragon Pharmaceuticals ("Underground Lab")	T-propionate T-phenylpropionate
66	Testabol Propionate	T-propionate	oily solution for i.m. application	100 mg/mL	British Dragon Pharmaceuticals ("Underground Lab")	T-propionate, T-phenylpropionate T-enantate
67	Trenabol	Trenbolone-acetate	oily solution for i.m. application	75 mg/mL	British Dragon Pharmaceuticals ("Underground Lab")	T-propionate, T-phenylpropionate Boldenone-undecylenate
68	Trenabol Depot	Trenbolone-hexahydrobenzyl-carbonate	oily solution for i.m. application	100 mg/mL	British Dragon Pharmaceuticals ("Underground Lab")	T-propionate, T-phenylpropionate Boldenone-undecylenate
69	Tri-Trenabol 150	Trenbolone-acetate, Trenbolone-hexa-hydrobenzyl-carbonate, T-enantate	oily solution for i.m. application	each 50 mg/mL	British Dragon Pharmaceuticals ("Underground Lab")	Trenbolone-enantate T-propionate, T-phenylpropionate T-enantate
70	Trenabol 200	Trenbolone-enantate	oily solution for i.m. application	200 mg/mL	British Dragon Pharmaceuticals ("Underground Lab")	Trenbolone-enantate T-propionate, T-phenylpropionate T-enantate

addition, two unlabeled plastic bags were confiscated, each containing approximately 5 g of a colorless powder, along with agents with anti-estrogenic activity (tamoxifen and clomiphene), drugs to stimulate sexual behavior (sildenafil and tadalafil), yohimbine, caffeine, and liothyronine.

Sample preparation

LC–MS–MS. After homogenization, aliquots of 5–50 mg of each compound or drug (except for hCG) were dissolved in 10 mL of methanol with the support of an ultrasonic bath. Remaining residues were removed by centrifugation, and supernatants were diluted (1:9) with methanol before injection into the LC–MS–MS system.

GC–MS and GC–MS-NPD. The unknown white powder was treated accordingly, but also analyzed using GC–MS and GC–MS-NPD. For the latter, no further derivatization was conducted, but for conventional GC–MS, the analyte was treated with *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA, Macherey-Nagel, Düren, Germany), which would form the trimethylsilyl derivative in the presence of reactive hydroxyl functions or amino residues. Therefore, 100 µL of the methanolic solution was evaporated to dryness, reconstituted in 100 µL of MSTFA, and heated at 60°C for 10 min (12,13).

Analytical methods

All drug preparations were subjected to LC–MS–MS analyses. An Agilent 1100 series HPLC (Waldbronn, Germany) interfaced via electrospray to an Applied Biosystems API 2000 QTrap analyzer (Darmstadt, Germany) was employed. The LC was equipped with a Zorbax XDB-C_8 analytical column (4.6 × 150 mm, 5-µm particle size), and eluents used were 5 mM ammonium acetate containing 0.1% acetic acid (eluent A) and acetonitrile (eluent B). At a flow rate of 800 µL/min (post-column split of 1:5), two different gradients were used to chromatographically separate target analytes. Steroid esters were measured starting at 75% A decreasing to 5% A in 4 min and remaining at 5% A for an additional 8.6 min, adapting literature recommendations (14). In contrast, all other compounds having less hydrophobic proper-

Table II. Characteristics of Analytes as Obtained Using LC–MS–MS

Analyte	$[M+H]^+$ *m/z*	Ion-Transition	Collision Offset (V)	Declustering Potential (V)	Retention Time (min)
Boldenone-undecylenate	453	453–269	30	50	11.3
		453–135	30	50	
		453–121	30	50	
Fluoxymesterone	337	337–317	35	50	7.6
		337–299	35	50	
		337–281	35	50	
Mesterolone	305	305–287	30	50	9.4
		305–269	30	50	
		305–229	30	50	
Metandienone	301	301–283	30	50	8.9
		301–135	30	50	
		301–121	30	50	
Methyltestosterone	303	303–28	30	50	8.9
		303–109	30	50	
		303–97	30	50	
Nandrolone-decanoate	429	429–109	35	50	12.6
		429–91	35	50	
Nandrolone-phenylpropionate	407	407–275	30	50	8.3
		407–257	30	50	
		407–105	30	50	
Oxymetholone	333	333–297	30	50	10.3
		333–279	30	50	
		333–159	30	50	
Stanozolol	329	329–105	50	50	7.3
		329–95	50	50	
		329–81	50	50	
Testosterone-propionate	345	345–253	26	50	7.7
		345–109	35	50	
		345–97	35	50	
Testosterone-phenylpropionate	421	421–253	25	50	8.3
		421–109	35	50	
		421–97	35	50	
Testosterone-isocaproate	387	387–253	25	50	9.2
		387–109	35	50	
		387–97	35	50	
Testosterone-decanoate	443	443–253	25	50	13.1
		443–109	35	50	
		443–97	35	50	
Testosterone-enantate	401	401–253	25	50	9.8
		401–109	35	50	
		401–97	35	50	
Testosterone-cypionate	413	413–253	25	50	10.1
		413–109	35	50	
		413–97	35	50	
Trenbolone-enantate	383	383–271	30	50	9.3
		383–253	30	50	
		383–225	30	50	

Continued

ties were analyzed starting at 95% A, decreasing to 5% A within 8 min, and remaining at 5% A for an additional 5 min to check for the presence of potential conjugates. The MS was operated in positive electrospray ionization (ESI) mode using a spray voltage of 5500 V. Full scan MS spectra and three selected ion transitions for each of the respective analytes and/or product ion spectra were recorded simultaneously, which provided unambiguous information on the identity of the compounds as compared to reference material and database spectra. Diagnostic product ions of the characterized compounds are listed in Table II.

GC–MS and GC–MS-NPD were utilized to provide additional information on the unknown colorless powder with and without derivatization, employing commonly accepted doping control analytical methods. Both instruments were Agilent 6890/5973 GC–MSD systems, one of which was equipped with an additional NPD. The GC–MS-NPD system was equipped with two HP5MS GC columns (Agilent, Waldbronn, Germany), which were directed from the injector to the MS or NPD detector, respectively. Thus, a single injection provided MS and NPD information on the measured specimen, and detected compounds were evaluated using the data obtained from both methods. The MS was operated in full scan MS mode covering the range of *m/z* 30–800.

Results and Discussion

Certain drugs and compounds confiscated within the context of house searches were analyzed using state-of-the-art chromatographic–mass spectrometric methods. In total, 70 products were measured in order to probe for authenticity of their content because differentiation between the original pharmaceutical packaging and faked boxes was not possible by visual inspection. Aliquots were taken from each batch number. The results of all analyses are summarized in Table I, sorted by findings in houses of different individuals.

Anabolic steroids

Out of 48 steroidal compounds, 17 (35.4%) did not or did not only contain the declared ingredients. Except for two products, compounds distributed by British Dragon Pharmaceuticals were found to comprise incorrect compositions. For instance, items 67–70 (Table I) were supposed to contain either trenbolone acetate, trenbolone hexyhydrobenzyl carbonate, or trenbolone enantate, but were composed of testosterone propionate, testosterone phenylpropionate, and either boldenone undecylenate or trenbolone enantate and testosterone enantate. Testosterone-derived drugs (items 65 and 66) such as the cypionate or propionate were found to be mixtures of testosterone propionate and phenylpropionate or testosterone propionate, phenylpropionate, and enantate, respectively. The advertised metenolone enantate (item 63) was identified as a pool of nandrolone decanoate, nandrolone phenylpropionate, testosterone propionate, testosterone phenylpropionate, and testosterone enantate, which also resembled the composition of item 62 (labeled as nandrolone decoanoate), except for nandrolone phenylpropionate. Authentic contents of products provided by British Dragon Pharmaceuticals were determined in items 61 (boldenone undecylenate) and 64 (stanozolol) only.

Sustanon 250 (Table I, items 3, 21, and 42–48) was labeled as produced in Pakistan and Egypt. The drug manufactured in Pakistan was identified as a mixture of the declared ingredients, while the Egyptian product comprised testosterone propionate, phenylpropionate, and cypionate [i.e., was lacking two of the labeled compounds (testosterone isocaproate and decanoate) but contained the non-declared testosterone cypionate]. Cidotestone (Table I, items 30 and 31) was labeled as containing testosterone enantate, but in one of the measured batches, testosterone cypionate was also observed. Three batches of "Anabol tablets" (all produced in Thailand) were analyzed, two of which contained the announced substance metandienone (Table I, items 9 and 28) and the other methyltestosterone only (item 8). In addition, another agent termed Naposim (Table I, item 39) was supposed to contain metandienone but also comprised methyltestosterone. Three batches of NORMA nandrolone decanoate were found to contain testos-

Table II. Characteristics of Analytes as Obtained Using LC–MS–MS *(Continued)*

Analyte	[M+H]$^+$ *m/z*	Ion-Transition	Collision Offset (V)	Declustering Potential (V)	Retention Time (min)
Sildenafil	475	475–311	35	50	6.8
		475–283	35	50	
		475–99	35	50	
Yohimbine	355	335–224	35	50	6.2
		335–212	35	50	
		335–144	35	50	
Tamoxifen	372	372–327	35	50	9.9
		372–129	35	50	
		372–91	35	50	
Clomiphene	407	407–297	35	50	9.3
		407–241	35	50	
		407–100	35	50	
Caffeine	195	195–123	35	50	5.2
		195–110	35	50	
		195–83	35	50	
Liothyronine	652	652–606	35	50	6.7
		652–508	35	50	
		652–479	35	50	

terone enantate (Table I, items 19 and 38) or testosterone enantate plus the respective cypionate (item 20), whereas another product presumably containing nandrolone decanoate (Decabol 250, Table I, item 62) consisted of nandrolone decanoate, testosterone propionate, testosterone phenylpropionate, and testosterone enantate. Moreover, Primobol 100 (Table I, item 63) contained five compounds not declared on its label. Instead of metenolone enantate, LC–MS–MS proved the presence of nandrolone decanoate, nandrolone phenylpropionate, testosterone propionate, testosterone phenylpropionate, and testosterone enantate.

Drugs stimulating sexual behavior

Eight batches of drugs based on selective 5-phosphodiesterase inhibitors such as sildenafil or taladafil were confiscated and analyzed (Table I, items 1, 2, 4, 5, 29, 36, 37, and 56). One representative (item 29, Cialis), which was supposed to contain tadalafil, was identified as an adulteration containing sildenafil.

Agents with anti-estrogenic activity

Two drugs with anti-estrogenic activity (tamoxifen and clomiphene, Table I, items 23, 49, and 50 and 32, respectively), presumably used to counteract the side effects of anabolic steroid misuse and also to reduce normal conversions of endogenously produced testosterone into estrogens (i.e., to increase the level of naturally produced testosterone by partial inhibition of its degradation) were confiscated.

Other compounds

In addition to the previously mentioned drugs relevant for doping controls, caffeine, yohimbine, and unlabeled bags containing a colorless powder were found in the context of the house searches. Caffeine and yohimbine (Table I, items 16 and 17 and 15, 24, and 60, respectively) were determined in respective products.

House searches conducted by police authorities are always initiated by strong suspicion and probable cause. Hence, the discovery of unlabeled, colorless powders (Table I, items 26 and

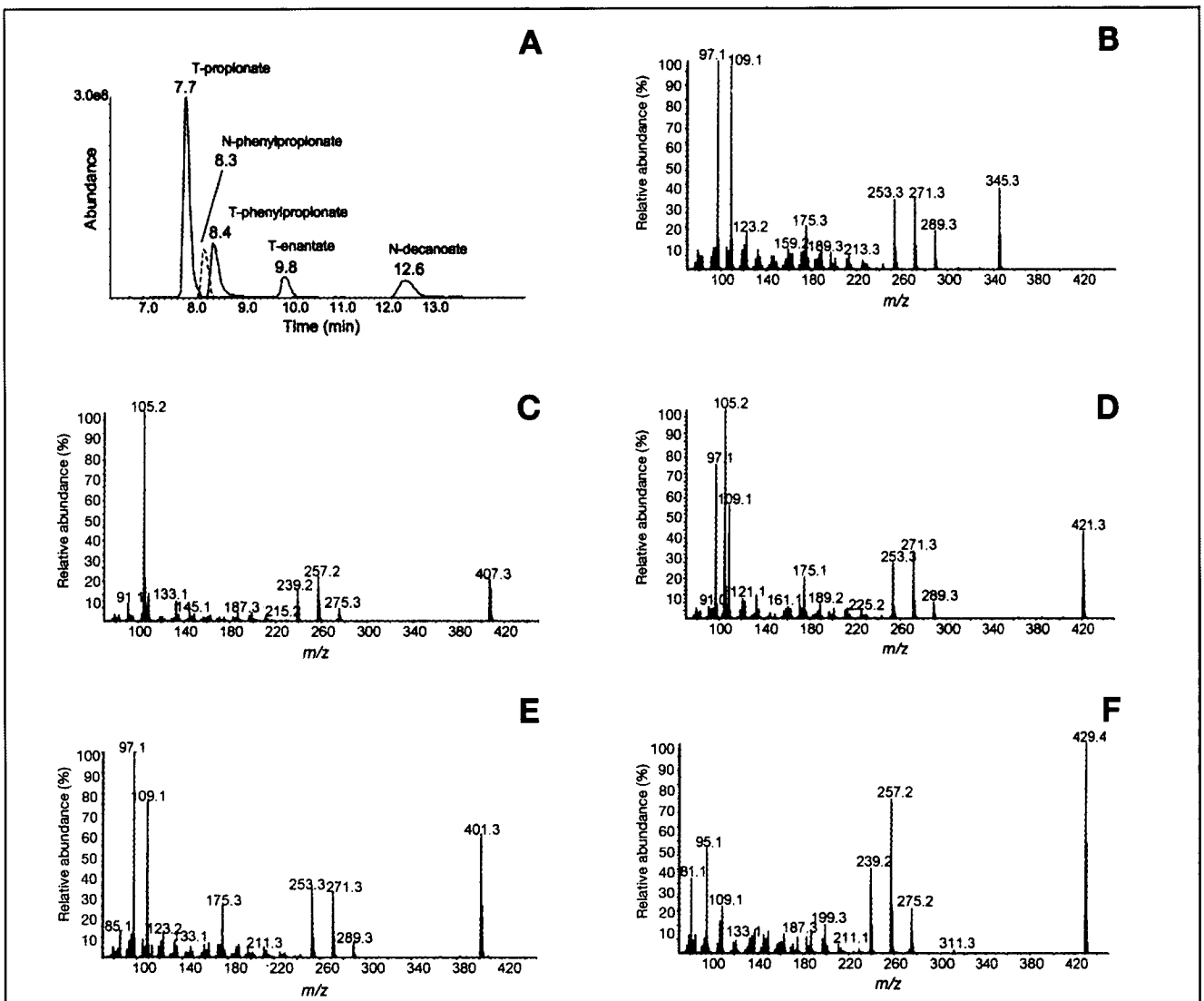

Figure 1. LC–ESI-MS chromatogram (A) and product ion mass spectra (B–F) of a drug supposedly containing metenolone enantate. Retention times and product ion mass spectra, however, revealed the presence of testosterone propionate (B), nandrolone phenylpropionate (C), testosterone phenylpropionate (D), testosterone enantate (E), and nandrolone decanoate (F).

27) initiated detailed investigations into whether the substances were relevant according to the controlled substances legislation. The compounds were subjected to LC–MS–MS and GC–MS-NPD with and without derivatization, and the latter strategy provided informative EI-mass spectra that allowed the unambiguous identification of gamma-aminobutyric acid (GABA) after comparison to reference material.

Analytical evidence

Proofs of compound identities were obtained using modern chromatographic–mass spectrometric techniques. All compounds were subjected to LC–MS–MS, and the unknown colorless powder was additionally analyzed using GC–MS-NPD with and without chemical derivatization. In Figure 1A is presented the LC–MS–MS chromatogram of item 63, which was supposed to contain metenolone enantate, but the composition of which was identified as nandrolone decanoate, nandrolone phenylpropionate, testosterone propionate, testosterone phenylpropionate, and testosterone enantate. Respective product ion mass spectra of the detected substances are illustrated in Figures 1B–F. For all steroidal compounds, identification was accomplished using three diagnostic product ions obtained after positive ESI followed by collision-induced dissociation (Table I). In addition, comparison of chromatographic retention times with reference material was utilized to substantiate the characterization of each compound.

Items 26 and 27 (Table I) were identified as γ-aminobutyric acid using GC–MS-NPD with and without derivatization. In Figure 2 are presented the chromatograms and EI mass spectra of trimethylsilylated products of aliquots of both batches (Figures 2A and B) in comparison to the reference material analyzed under identical conditions (Figure 2C). The use of trimethylsilylation (TMS) enabled the unambiguous differentiation of GABA from its structurally related analogue γ-hydroxybutyric acid (GHB). While the latter is converted to a *bis*-TMS derivative only, GABA gives rise to the *tris*-TMS analyte, which is unequivocally identified by fragment ions observed, for instance at *m/z* 304 (M^+–15).

Conclusions

The analysis of 70 compounds confiscated in house searches in Germany revealed the presence of 18 (25.7%) boxes with contents deviating from the declared ingredients. Drugs and their adulterations originated, according to their labels, from different countries such as Egypt, Germany, Greece, India, Israel, Italy, Pakistan, Spain, Thailand, and the United States. A visual inspection of faked therapeutics did not allow a differentiation between original products and counterfeits. Batches of drugs supposedly prepared by the same manufacturer were found to have different contents, which was the major reason for analyzing aliquots of all provided batches. The difficulty of unambiguously distinguishing counterfeit preparations from authentic drugs originated from several aspects such as the frequently observed re-use of original packaging. Paper or plastic drug containers officially designed for the sale and distribution of a single ampoule were, for instance, filled with up to five ampoules. Moreover, copies of cardboard packaging can be of the highest quality, and only the comparison of batch and production numbers found on confiscated drugs

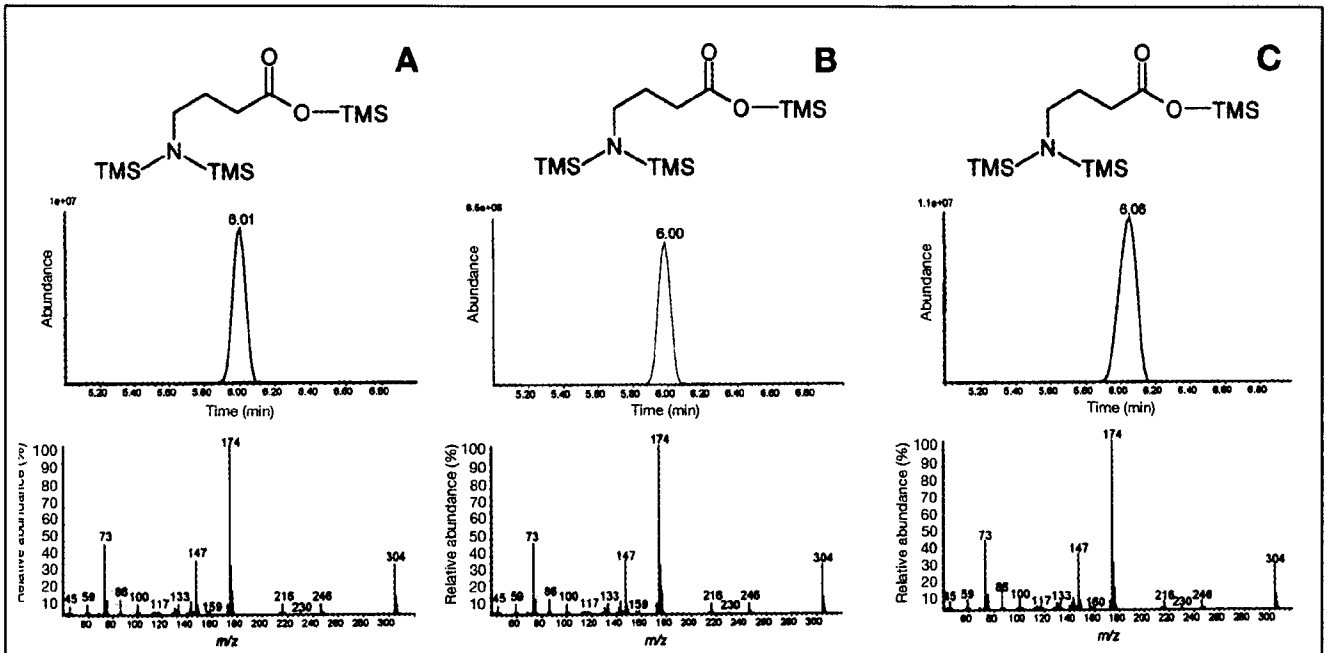

Figure 2. GC–EI-MS chromatograms and mass spectra of aliquots of the confiscated colorless powder after trimethylsilylation (TMS). The suspicious samples identified as GABA are presented in A and B, and analysis of the reference material of GABA yielded the chromatogram and mass spectrum depicted in C. The presence of the ion at *m/z* 304 (M^+ –15) of the *tris*-TMS derivative allows the unambiguous distinction of GABA from related compounds such as γ-hydroxybutric acid, which would yield only a corresponding *bis*-TMS analogue.

with those provided by the manufacturer might indicate a faked product. However, the possibility that original products could contain agents different from those indicated on the label was not ruled out with the present study but deemed unlikely. The majority of faked drugs concerned anabolic steroids (17), but compounds stimulating sexual behaviour were also subject to adulteration.

In all cases, a qualitative analysis was performed, but no quantitation of respective ingredients, as the aim of the study was to identify ingredients of drugs sold on the black market. Hence, drugs containing the declared product may also be faked with less or more amounts of agents, and thus resemble another level of risks that athletes take when using such compounds. Related and suspected health issues have been frequently discussed in the literature (11,17,18), and future studies regarding the amount of pharmacologically active compounds in black market drug preparations shall provide further details about the occurrence and composition of faked therapeutics.

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