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Formation of Nitrogen Derivatives through the Terpenoids

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ABSTRACT: The presence of nitrogen in the molecule is usually accompanied either by the appearance of a new activity or the intensification of original activity characteristic for the native terpenoids. This maintains alive the scientific interest in the synthesis of such compounds. The present communication put into discussion the recently elaborated methods for preparation of the nitrogen-containing terpenic compounds.

KEYWORDS: synthesis, nitrogen-containing compounds, terpenoids, Beckmann rearrangement.

I. INTRODUCTION

Many terpenes exhibit various biological activities [1, 2]. In a series of articles it has been reported on the appearance of a new activity or the intensification of the original activity that accompanies the introduction of nitrogen in the molecules of native terpenoids. Therefore the synthesis of the nitrogen-containing terpenic compounds is of great interest for further studies of their biological activity.

Synthesis of the nitrogenated derivatives of drimanes and homodrimanes

The nitrogen-containing sesquiterpenic compounds and their biological activity represent a poorly studied area of terpenoid chemistry. The first synthesis of the homodrimanic nitrogen derivatives was reported by Grant P.K. et al. in 1983 [3]. Oxidative degradation of manool (1) [4] gives the intramolecular acetals (2) and (3). The former possesses a powerful ambr-type odour and is being used in the perfumery industry. In this light it was interesting to examine the synthesis of the nitrogen analogues (4) and (5). Reaction of the methylene ketone (6), in turn obtained from the permanganate oxidation of manool (1), with hydroxylamine gave the isomeric oximes (7) and (8) in 5:2 ratio. Their stereochemistry was assigned on the basis of the corresponding amides obtained under Beckmann rearrangement conditions. By direct treating of the oximes with thionyl chloride only low yields of amides were obtained, while by using the base-promoted rearrangement of the tosylate derivatives the yields were greatly increased.[1,2]

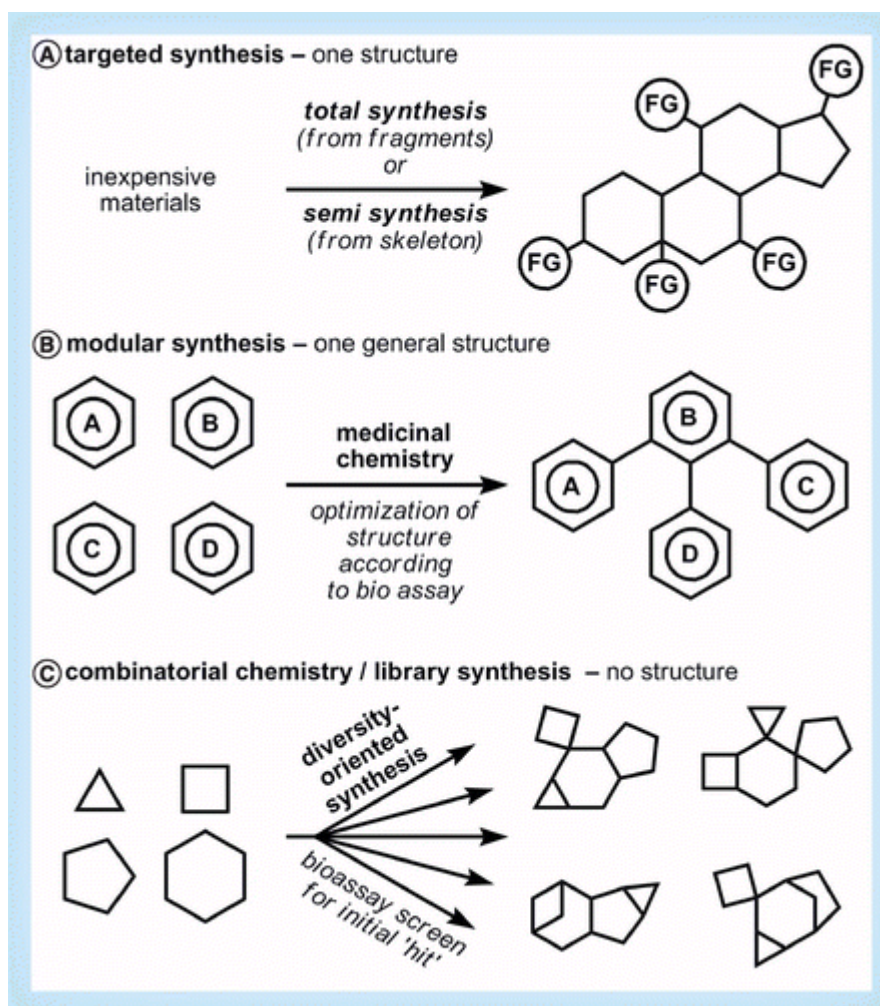
The tosyl derivative (7a) of the less polar oxime (7) furnished the amide (9) in quantitative yield upon treatment with dilute base at room temperature. Since it is known, that Beckmann rearrangement proceeds by a stereospecific *anti*-migration, the *E*-configuration for the oxime (7) has been established. The more polar (O-tosyl) oxime (8a) required more forcing conditions to effect the rearrangement and gave the amide (10) in 27% yield. Since the amide structure was established to be as depicted in formula (10), this pointed to *Z*-stereochemistry of the parent oxime (8). The rearrangement of the oxime tosylates under acidic conditions gave the same amide product (9), thus reflecting the facile isomerization of the less stable *Z*- (O-tosyl)oxime (8a) prior to rearrangement [5].

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Later the synthesis was reported by Urones, J.G. et al. [6] describing the use of 12-acetoxy-7,9(11)-drimandien (11), that was in turn prepared from methyl zamoranate (12), as a precursor for C-9 nitrogenated drimanes (Scheme 2). Dien (11) reacts with *m*-CPBA in a regio- and stereoselective way, affording the epoxide mixture of compounds (13) and (14) [7]. On ulterior derivatisation the α -epoxide afforded carbonates (15) and (17) and carbamates (16) and (18). Alkaline hydrolysis of acetate (18) by using a 2N NaOH solution in dioxan (1/1) afforded the corresponding alcohol (19) in 96% yield [8]. Extreme reaction conditions, including saturated solution of KOH and 1,2-ethanediol at 70° C [9] led to the difficultly isolable amino diol (20) in 90% yield. Its treatment with Ac₂O/Py [10] gave the spirodihydrooxazole acetate (21) in 84% yield. In virtue of the amino alcohol high reactivity, the protection of its amino group was required. Hence (21) was treated with (Boc)₂O [11], yielding the N-Boc derivative (22) in 73% yield. Since the latter was resistant to hydrolysis, it could be reduced with DIBAL-H, furnishing diol (23) in good yield (73%). [3,4]

Reagents:

a) aqueous 2N NaOH/1,4-dioxane 1/1, 96%;

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b) saturated KOH in H₂O, 1,2-ethanediol, 70°C, 90%;

c) Ac₂O, Py, 84%;

d) (Boc)₂O, Et₃N, DMAP, THF, 73%;

e) DIBAL-H, CH₂Cl₂, -78°C, 73%.

New synthetic strategies to prepare natural drimanes from (-)-sclareol (24) have been reported by Barrero and co-workers [12]. Thus the preparation of natural 9,11-drimen-8 α -ol (25) through the nitrogen-containing compounds is described. Synthesis of compound (25) started with the homodrimanic acid (26), in turn obtained from sclareol (24) in 75% overall yield by a two-step sequence [13].

The Curtius rearrangement of the acyl azide derived from (26) represented the key-step in the discussed synthesis. Treatment of (26) with diphenylphosphorylazide (DPPA) in the presence of triethylamine with subsequent reflux in benzene gave the isocyanate (27) [14]. All attempts to transform the latter into the corresponding amine were unsuccessful: hydrolysis of the isocyanate afforded only a very stable cyclic carbamate. Therefore the way was chosen to reduce compound (27) till the formamide (28) that was next treated with potassium hydroxide in methanol to afford the hydroxyacetamide (29) or the aminoalcohol (30), respectively, depending upon the reaction temperature. Then, the transformation of amine (30) into (25) was approached. First of all, diazotization of the amine group was attempted. The main observations were that the amine (30) remained unaltered when it was treated at 0 °C with sodium nitrite and hydrochloric acid, while at room temperature its decomposition occurred. Hofmann elimination turned out to be also unsuccessful. Treatment of alcohol (30) with potassium *tert*-butoxide in dimethylsulfoxide after exhaustive methylation afforded the methoxyamine (31). In this way the hydroxyl group of compound (28) was protected by treating it with ethyl vinyl ether to give (32). Saponification of the latter consistently afforded the amine (33), which underwent elimination after exhaustive methylation on treatment under basic conditions yielding (34). The removal of protection subsequently gave (25) (Scheme 3).

Reagents:

1. OsO₄, NaIO₄, *t*-BuOH, 45°C, 6h.; 2. Jones' oxidation, acetone, 0°C, 45 min (75% overall yield);
1. DPPA (1.1 eq), Et₃N (1.1 eq), Dioxan, 0°C, 1.5 h; 2. Benzene, reflux;
- Na BH₄ (3 eq), Et OH, 0°C, 30 min. (80%);
- KOH, MeOH, rt, 6 h (96%);
- KOH, MeOH, reflux, 12 h (95%);
1. Excess MeI, *t*-BuOMe; 2. *t*-BuOK (1.4 eq), DMSO (80%);
- ethyl vinyl ether (8 eq), CSA (0.5 eq), CH₂Cl₂, rt, 25 h (75%);
- KOH, MeOH, reflux, 2 h (91%);
1. excess MeI, *t*-BuOMe; 2. *t*-BuOK (2.7 eq), DMSO (85%);
- AcOH, MeOH, rt, 2 h (95%).

Reagents:

- PO, DMSO, 20°C, 95%;
- NHOH·HCl; EtOH, Py, 95%;

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c) AcO, Py, 64%;

d) p-TsCl, Py, 90%;

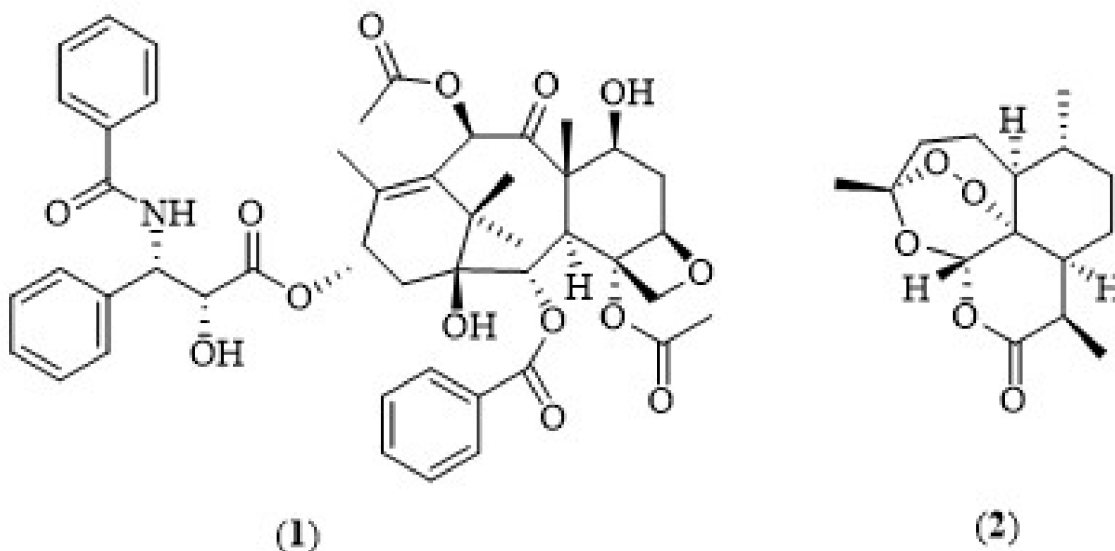
e) LiAlH₄, A⁵ ICl, Et O, 50%;

f) NaBH₄, CoCl · 6H₂O, MeOH, 20°C, 91%.²

Therefore, it seemed interesting to synthesize the amino- analog of drimenol in order to study its biological properties.

II. DISCUSSION

We accomplished the synthesis of 11-aminodrim-7-ene (36) from drimenol (35) in four steps [15] (Scheme 4). Drimenol (35) was oxidized into drimenal (37) in 95% yield *via* phosphoric anhydride activated dimethylsulfoxide, as previously reported [16]. Drimenal oxime (38) was obtained on interaction of drimenal (37) with hydroxyamine hydrochloride in the ethanol-pyridine mixture of solvents. According to TLC, the reaction product consisted of a mixture of *Z*- and *E*-isomers. The oxime of 14,15-bisnorlabd-8-(17)-en-13-one (7) was used as reference to show that the less polar isomer had the *E*-configuration [3]. Since the *E*-configuration of (7) is energetically more favourable, the predominant isomer in the mixture should most probably be the *E*-isomer. In the drimenal oxime (38) obtained by us the above-mentioned less polar isomer predominated. Its content in the mixture after recrystallization from hexane was 80%, the ratio of *Z*- and *E*-isomers being approximately 1:4. Next we investigated the production of drimenylamine (36) *via* the reduction of drimenal oxime (38) by various methods [17-20].



Compound (36) could not be synthesized in satisfactory yield by the reduction of drimenal oxime (38), that is why we decided to convert (38) into the corresponding nitrile (39) and then reduce it to the amine (36). Several methods have been employed by us in order to synthesize (39) [21-27]. As a result, we found as acceptable methods for synthesizing (39) the reactions of (38) with *p*-TsCl or Ac₂O in pyridine. The target- product, 11-aminodrim-7-ene (36), was obtained in 50% yield by refluxing the hydroxyamine (38) with LiAlH₄ in Et₂O in the presence of anhydrous AlCl₃ [28]. The reduction of nitrile (39) by NaBH₄, CoCl · 6H₂O in CH₃OH produced compounds (36) and 7,8-dihydro-11-4-2

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2,3-aminodrimane (40), as a mixture of water-soluble hydrochlorides. The ^1H NMR-spectrum of the mixture indicated on a 2:1 ratio of the hydrochlorides of (36) and (40). The pure compound (36) and its mixture with (40), synthesized by us, are of interest as potentially endowed with biological activity.[5,6]

Reagents:

- NH₄OH·HCl, EtOH, Py;
- Ac₂O/Py, 105-110°C;
- 86% H₃PO₄, 60-70°C, 82%;
- p*-TsCl, Py, 90%; e) CH₃CN, Δ;
- p*-TsON, 95%;
- 10% KOH, MeOH, 95%;
- Al₂O₃, 58%.

The synthesis of amide (41) *via* Beckmann rearrangement of oxime (42) of 11-dihomodriman-8 α -ol-12-one (43) was the main our goal we pursued [29]. Hydroxyketone (43) is readily available, being obtained from norambreinolide (44) by the method described by us [30]. Oxime (42) was prepared from compound (43) by its reaction with NH₄OH·HCl in an ethanol-pyridine mixture of solvents. Compound (42) represented a mixture of *Z*- and *E*-isomers, according to its TLC data and ^1H , ^{13}C , and ^{15}N NMR spectra. In virtue of easy conversion of *Z*- into the *E*-isomer as a result of the fact that the latter is energetically more favorable [3], we used (42) for the reactions as a mixture of its *Z*- and *E*-isomers. It was found that on interaction of the oxime (42) with acetic anhydride in pyridine the oxime acetate (45) along with a small amount of the mixture of isomeric dehydrated oxime acetates (46)-(48) were formed. On heating of the solution of the oxime (42) in 86% H₃PO₄ the elimination of water occurred giving 1,2-oxazine (49). Oxime (42) interacts with *p*-tosyl chloride in pyridine affording the oxime tosylate (50). The latter rearranges under reflux in acetonitrile, according to the Beckmann transposition, with the elimination of the water and *p*-toluene sulfonic acid, giving the unsaturated amide (51). The reaction of compound (51) with *p*-TsOH leads to the corresponding salt of cyclic 1,3-oxazine (52) formation, which upon treatment with a methanolic solution of potassiumhydroxide furnished compound (53).

III. RESULTS

The new nitrogen containing drimanic compounds, the 1,2,6-oxazine and N-pyrroline oxide derivatives were obtained [31], which are of interest as compounds potentially endowed with interesting biological properties. 11-dihomodriman-8 α -ol-12-one (43) was prepared according to the reported protocol [30] and subjected to the dehydration in the presence of the „Amberlist-15” ionite. As result ketone (54) was obtained, which was transformed into oxime (55) by interaction with NH₂OH·HCl.

- Reagents: a) Amberlist-15, CH₂Cl₂, 20°C, 20 h, 70%;
- NH₂OH·HCl, EtOH, Py, 98%;
 - H₃PO₄, (64:65)=36%:56%; CF₃CO₂H, (64:65)=30%:48%.

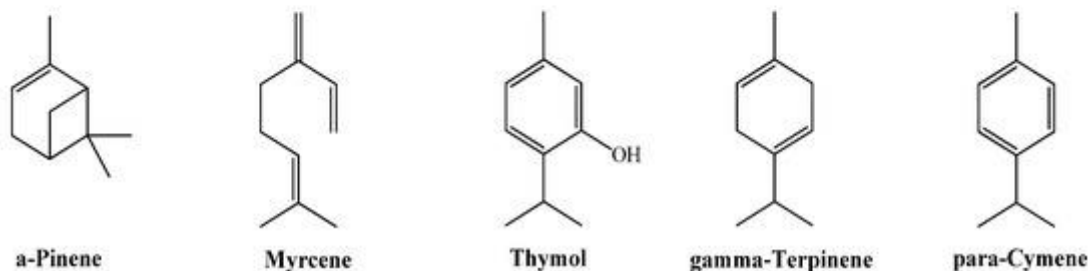
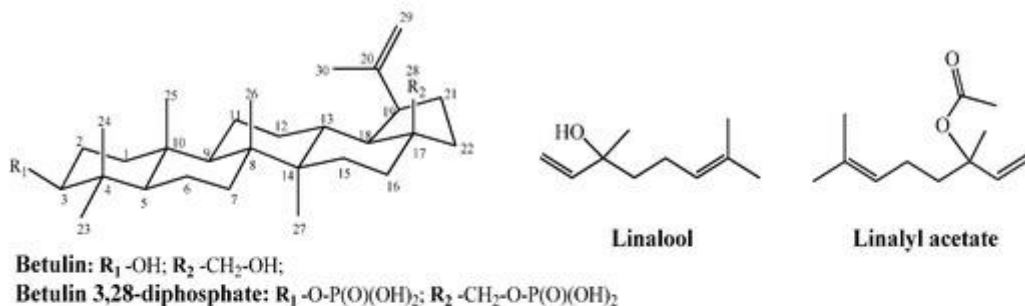
By heating at 70-80°C a solution of the oxime (55) in 86% H₃PO₄, the intramolecular cyclization occurred, giving the mixture of (1S,2S,4a S,8aS)-2,5,5,8a-tetrametildecahidro-1H-nafto[1,2][5,6]-3-metil-4,5-dihidro-[1,2,6]-oxazine (56) and (1S,2S,4a S,8aS)-2,5,5,8a-tetrametildecahidro-1H-nafto[1,2-d]-2-metilpirolin-N-oxide (57). The same outcome was reached by heating the oxime (55) in CF₃CO₂H.[7,8]

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Reagents:

1. CTDL, CHCl₃, reflux, 21 h, (94%), 2. n-Bu SnH, AIBN, toluene 80°C, 15 min (quant), 3. DIBAL, THF, 0°C, 15 min (98%);
1. TBSCl, imidazole, DMF, 0°C to rt, 15 min (97%), 2. MCPBA, CHCl₃, 0°C, 24 h, (α : 62%, β : 30%);
1. TPAP, NMO, CHCl₃, rt, 3,5 h, 2. Ph P⁺CH OMeCl⁻, n-BuLi THF, 0°C², 10²min (60% in two steps);
1. TBAF, THF, 0°C to rt, 3 h (86%), 2. Dess-Martin periodinan CHCl₃, rt, 4 h;
- n-BuLi, THF, 0°C to rt, 1 h (48% in two steps α : β =4:1);
- MeLi, THF, 0°C, 10 min (72%, E:Z=4:1);
- NH₃, cat. AcOH, t-BuOH, rt, overnight [65% from (E), 60% from (Z)]; h) TBAF, THF, rt, 1,5 h, (89%).

Reagents:

- MeNH₂/NaBH₄;
- CH₂O;
- PCC/CH₂Cl₂;
- MeNH₂/NaBH₄;
- CH₂O;
- PCC/CH₂Cl₂;
- MeNH₂/NaBH₄;
- CH₂O.

Focusing on the preparation of the new diterpenoids of labdane series that contain a heterocyclic fragment of 10-oxa-3-azatricyclo[5.2.1.0^{1,5}]decene (93), the intramolecular [4+2]-cycloaddition reaction of quaternary ammonium salts

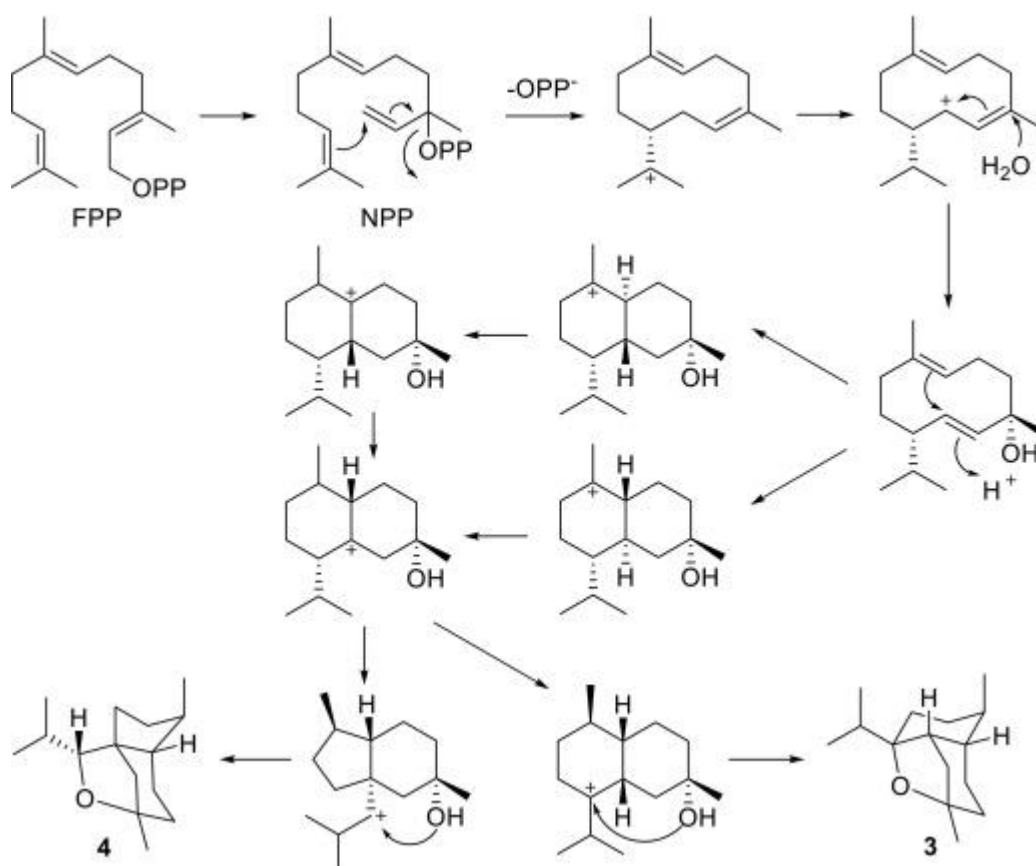
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obtained by quaternization with allyl, methallyl, or propargyl bromides of lambertian acid dialkylaminomethyl derivatives was investigated [36]. Kharitonov Yu.V. et al. [37] report on an interesting approach to the new heterocyclic derivatives of labdanoids that is based on the transformation of 15,16-epoxy labdadiene-15,16-dione (94).



The starting compound for this synthesis is readily obtained by oxidative transformations of accessible methyl lambertianate (79). The oxidation of furan labdanoid (79) with Jones' reagent gave rise to a mixture of the corresponding anhydride (94) and hydroxybutenolides (95) and (96) whose ratio depended on the reaction conditions. By reaction with secondary amines compound (94) gave new terpenyl-containing N-substituted maleimides (97) and (98) (Scheme 11). It is well-known that the reaction of maleic anhydride and its substituted analogs with hydrazines represents an efficient procedure for the preparation of pyridazinediones. The reaction of anhydride (94) with hydrazine hydrate occurred in acetic acid at room temperature and afforded a mixture of 3,6-dihydro-1,2,3,6-tetrahydropyridazine (99) and (N-amino)maleimide (100) (in 47 and 15% yield). The reaction of anhydride (94) with phenylhydrazine required more stringent conditions, since 3-hydroxy-1-phenyl-(2H)-pyridazin-6-one (101) and (N-amino)maleimide (102) could be obtained under boiling the reagent mixture in acetic acid in 22 and 38% yield, respectively. Thus diterpenoids of new structural type, labdanopyridazinediones, were prepared for the first time. [9,10]

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IV. CONCLUSION

The above-presented data demonstrate that lately the vast series of known natural terpenoids has been intensely supplemented by the nitrogen-containing metabolites of plant, microbial and animal origin. The unique structure of many so-called mixed metabolites, whose molecules include nitrogen, and their important biological properties make them attractive targets of the total synthesis. On the other hand, they can serve as plausible models for designing the molecules with useful functions.

Thus, the Scientific Interest remains opened to the exploration of new exciting facets of nitrogen-containing terpenoids.[11,12]

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