CHEMICAL COMPOSITION OF PLANT *CARLINA* SPECIES

Maciej Strzemski[1], Magdalena Wójciak-Kosior[1], Ireneusz Sowa[1], Jan Sawicki[1], Ewelina Rydzik-Strzemska[1], Aleksandra Bożyk[2], Ryszard Kocjan[1]*

[1]Department of Analytical Chemistry, Medical University of Lublin, Lublin, Poland
[2]Department of Pneumology, Oncology and Allergology, Medical University of Lublin, Lublin, Poland

*Corresponding author e-mail: maciej.strzemski@poczta.onet.pl

S u m m a r y. There are numerous historical data on the medicinal usage of plants from *Carlina* genus, and these plants have been still used in folk medicine in many countries; however, the research into their chemical composition is rare. According to literature, polyacetylenes, pentacyclic triterpenes, flavonoids and phenolic acids are the main classes of pharmacologically active compounds of *Carlina* plants. There are also reports on the presence of fatty acids, tannins and inulin. In the paper, the current state of knowledge on phytochemistry of *Carlina* genus is reviewed.
K e y w o r d s: *Carlina* species, triterpenes, essential oil, chlorogenic acid, flavonoids, fatty acids

INTRODUCTION

The genus of *Carlina* L. (Asteraceae Dum.) comprises over 30 species found in their natural habitat in Europe, North Africa and Asia up to Siberia (Tutin et al.1976; Kovanda 2002). Some species of the *Carlina* family have been used in folk medicine. *C. acaulis* L. and *C. acanthifolia* are the most significant among them; however, taxa such as *C. bibersteinii* Bernh. ex Hornem., *C. corymbosa* L., *C. vulgaris* L. and *C. utzka* Hacq were also used for medicinal purposes. Some species were also vegetal components of the human diet. All information about the usefulness and medical importance of *Carlina* mostly come from the historical and ethnobotanical sources because scientific research is rare (Strzemski et al., 2014).

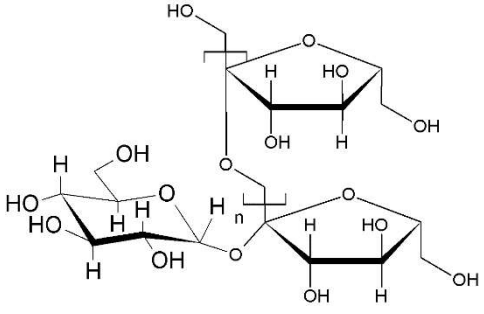
Dioscorides and Galen, who practiced medicine in ancient time, recommended the root of *Carlina* for the toothache mitigation, and herb for the treatment of various skin disorders. Moreover, they applied the plant to treat liver and spleen diseases, as well as an anthelmintic remedy. The *Carlina* root was described in Polish and Prussian pharmacopoeia (Pharmacopoeia Regni Poloniae 1817 and Pharmacopoeia Borussica 1799) as a diaphoretic, diuretic, laxative, anthelmintic, and menstruation stimulating drug.

Nowadays, the *Carlina* plants are applied as dermatological and gastrological remedies in ethnomedicine of many countries; however, the chemical composition and the pharmacological properties are insufficiently explored and poorly documented.

The aim of this paper was to summarize the current knowledge on the phytochemistry of *Carlina* genus.

Inulin

Inulin (Fig. 1) is a typical chemical constituent of plants from Asteraceae family, and is used as a diagnostic agent, prebiotic and component of diet supplements for diabetics (Kohlmünzer 2007). It is a polysaccharide composed of β-D-fructofuranose units combined through the β(2→1) bonds, and usually terminated with α-D-glucopyranose unit. The main saccharide of inulin is fructose.

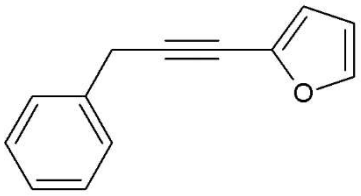


F i g u r e 1. Inulin

According to scientific reports, the root of *C. acaulis* contains about 20 % of inulin. (Stojanović-Radić et al. 2012, Đorđević et al. 2005, 2007 and 2012).

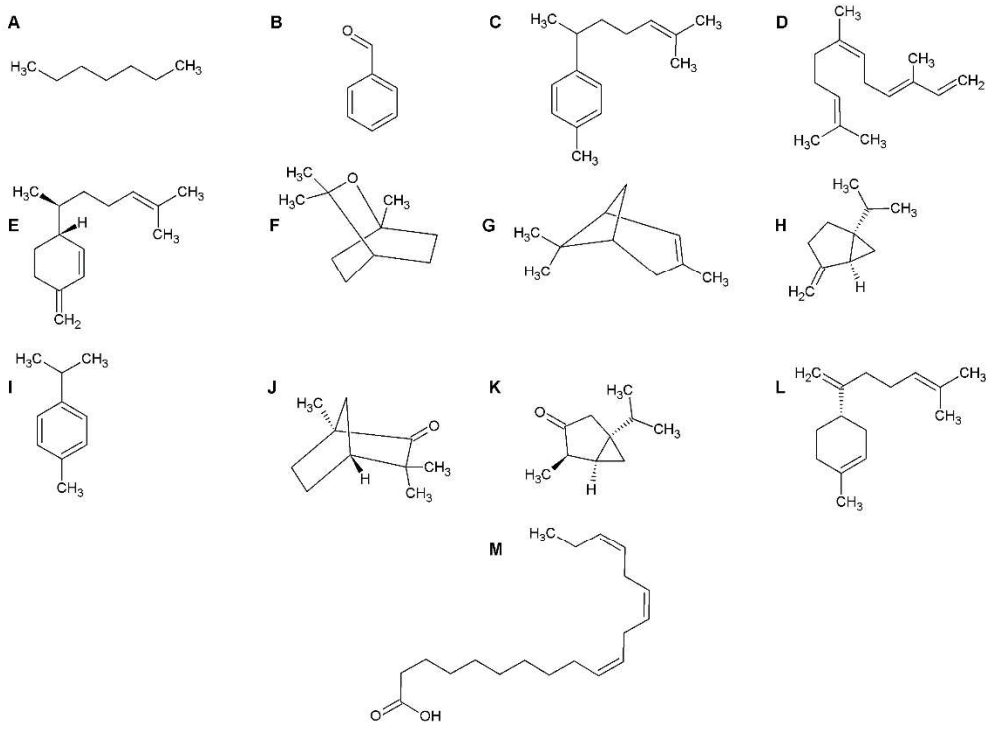
Essential oil

Carlina root is a typical oil material. *Oleum Carlinae* is a yellowish liquid with intensive narcotic smell. Its content ranges from 1 to 2% (Đorđević et al. 2012). Most of research refers to the material called *Carlinae radix* which is the mixture of *C. acaulis* and *C. acanthifolia* roots. The content of essential oil in that material is about 1.05% (Jović J, et al. 2012), and its main component is polyacetylene – carlina oxide (2-(3-phenylprop-1-ynyl)furan) (Fig. 2) (Stojanović-Radić et al. 2012, Đorđević et al. 2005, 2007, 2012, Herrmann et al. 2011, Kohlmünzer 2007, Chalchat et al. 1996) which constitutes up to 97.2% (Chalchat et al. 1996).



F i g u r e 2. Carlina oxide

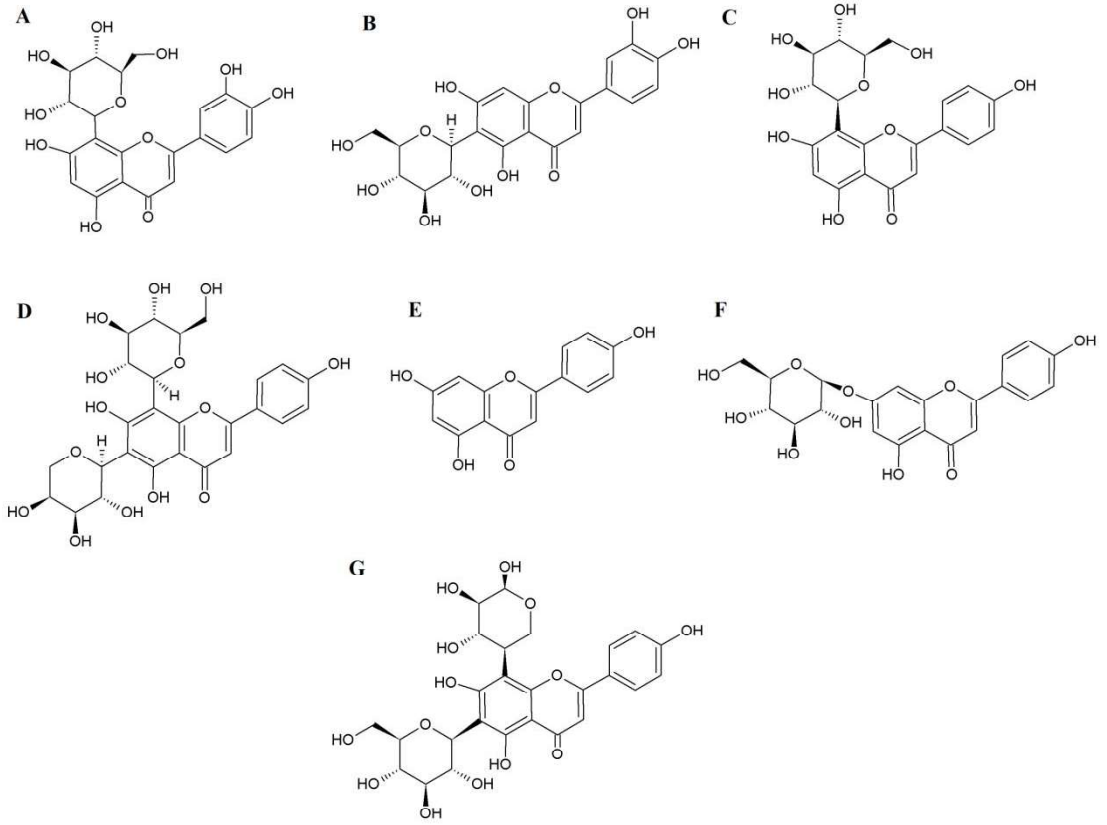
Other chemical compounds identified in the essential oil are heptane (0.5%), benzaldehyde (0.8%), *ar*-curcumene (0.6%), (*E,Z*)-α-farnesene (0.2%), β-sesquiphellandrene (0.2%), and trace amounts (<0.05%) of cineole (Chalchat et al. 1996), α-pinene, sabinene, *p*-cymene, fenchone, β-thujone, β-bisabolene oraz (Z,Z,Z)-9,12,15-octadecatrienoic acid (Stojanović-Radić et al. 2012). The structures of essential oil compounds are presented on Fig. 3.



F i g u r e 3. The chemical structures of *Carlina* essential oil components: heptane (A), benzaldehyde (B), arcurcumene (C), (E,Z)-α-farnesene (D), β-sesquiphellandrene (E), cineole (F),), α-pinene (G), sabinene (H), p-cymene (I), fenchone (J), β-thujone (K), β-bisabolene (L) and (Z,Z,Z)-9,12,15-octadecatrienoic acid (M).

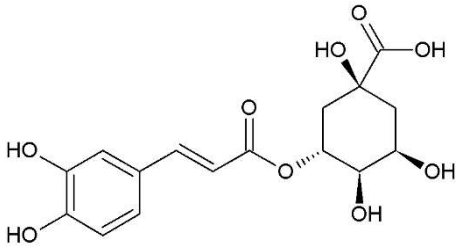
Phenolic compounds

Numerous phenolic compounds, including phenolic acids and flavonoids are found in herbs of various species from *Carlina* genus. C-glycosyl flavones such as orientin (0.32 %) (Fig. 4A), homoorientin (0.92 %) (Fig. 4B), vitexin (0.61 %) (Fig. 4C) and isoschaftoside (Fig. 4D), as well as apigenin (0.15 %) (Fig. 4E) and apigenin 7-O-glucoside (0.45 %) (Fig. 4F) were found in *C. acaulis* (Bohm and Stuessy 2001, Raynaud and Rasolojaona 1979). In *C. acanthifolia*, schaftoside (0.75 %) (Fig. 4G), homoorientin (0.91 %), orientin (0.26 %) and apigenin (0.22 %) were detected (Đorđević et al. 2012).



F i g u r e 4. The chemical structures of *Carlina* flawonoids: orientin (A), homoorientin (B), vitexin (C), isoschaftoside (D), apigenin (E), apigenin 7-O-glucoside (F), schaftoside (G).

Furthermore, the presence of chlorogenic acid (1.94 %) (Fig. 5) was con rmed in the herb *C. acaulis* (Jaiswal et al. 2011; Đorđević et al. 2012). The term 'chorogenic acid' refers to the mixture of various esters of qunic acid and trans-cynamonic acids such as caffeic, ferulic, sinapic, dimethoxycinnamic and p-cumaric acid, and the detailed pro le of chlorogenic acids in *C. acaulis* included the following compounds: 3-*O*-Caffeoylquinic acid (chlorogenic acid), 4-*O*-caffeoylquinic acid (cryptochlorogenic acid), 5-*O*-caffeoylquinic acid (neochlorogenic acid), *cis*-5-*O*-caffeoylquinic acid, caffeoyl-*epi*-quinic acid, 3-*O*-feruloylquinic acid, 5-*O*-feruloylquinic acid, *cis*-3-*O*-feruloylquinic acid, *cis*-4-*O*-feruloylquinic acid, *cis*-5-*O*-feruloylquinic acid, 5-*O*-*p*-coumaroylquinic acid, *cis*-5-*O*-*p*-coumaroylquinic acid, A *cis*-3,5-*O*-dicaffeoylquinic acid, A *cis*-3,4-*O*-dicaffeoylquinic acid, 4,5-*O*-dicaffeoylquinic acid, 4-*O*-feruloyl-5-*O*-caffeoylquinic acid and 3-*O*-caffeoyl-4-*O*-feruloylquinic acid (Jaiswal et al. 2011).



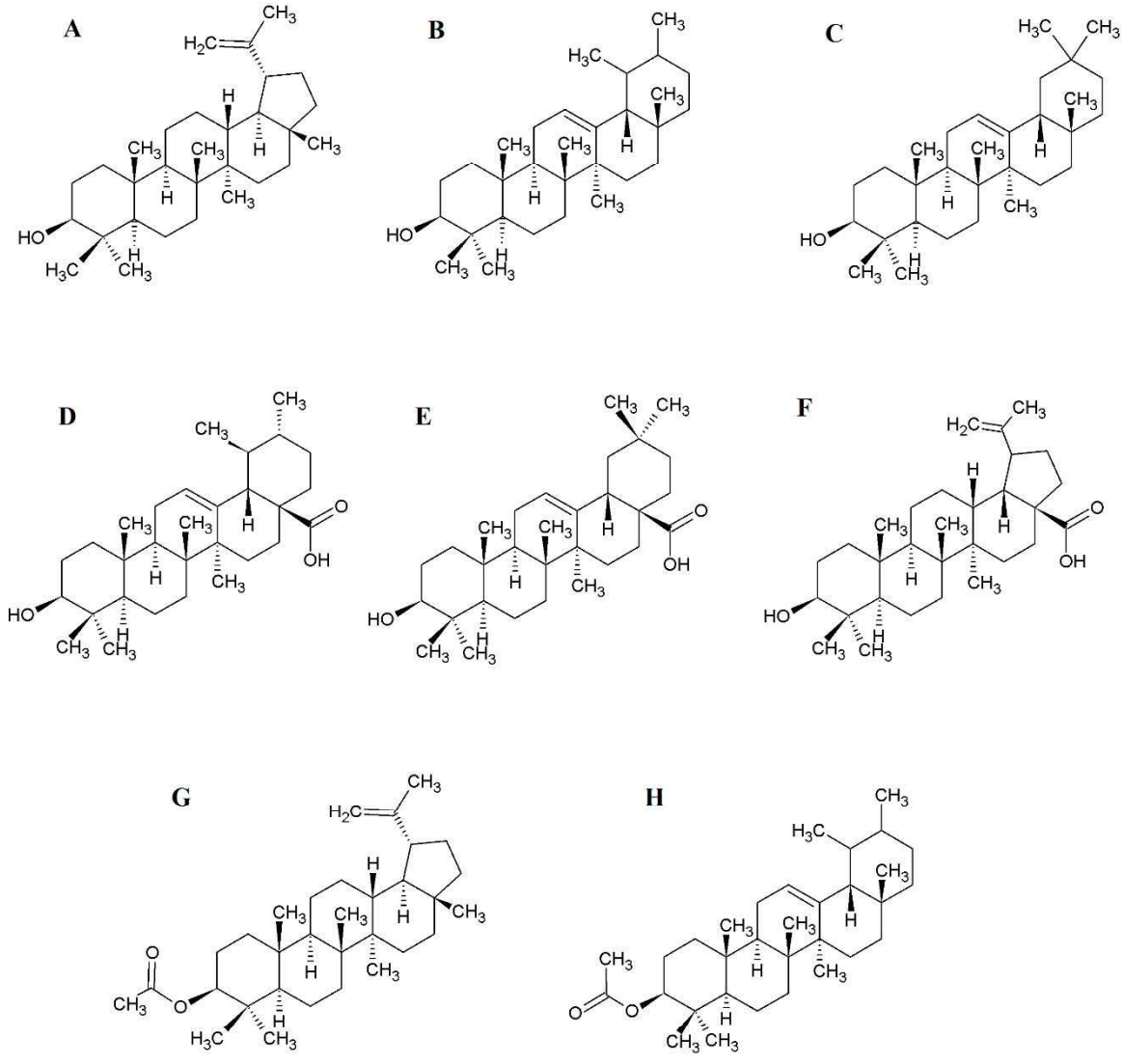
F i g u r e 5. Chlorogenic acid

The presence of tannins in *C. acaulis* roots is mentioned, too, however, there is no thorough experimental data.

Triterpenes

Triterpenes such as lupeol (Fig. 6A), α-amyrin (Fig. 6B) and β-amyrin (Fig. 6C) were identi ed in *C. corymbosa* var. *globosa* (Piozzi et al., 1975) and in *C. oligocephala* (Mausel and Kästner 1990). Moreover, Strzemski et al. (2016) carried out the detailed investigation of triterpene content in various species of *Carlina* genus including *C. vulgaris* L., *C. acaulis* L., *C. acaulis* subsp. *caulescens* (Lam.) Schübl. & G. Martens, *C.*

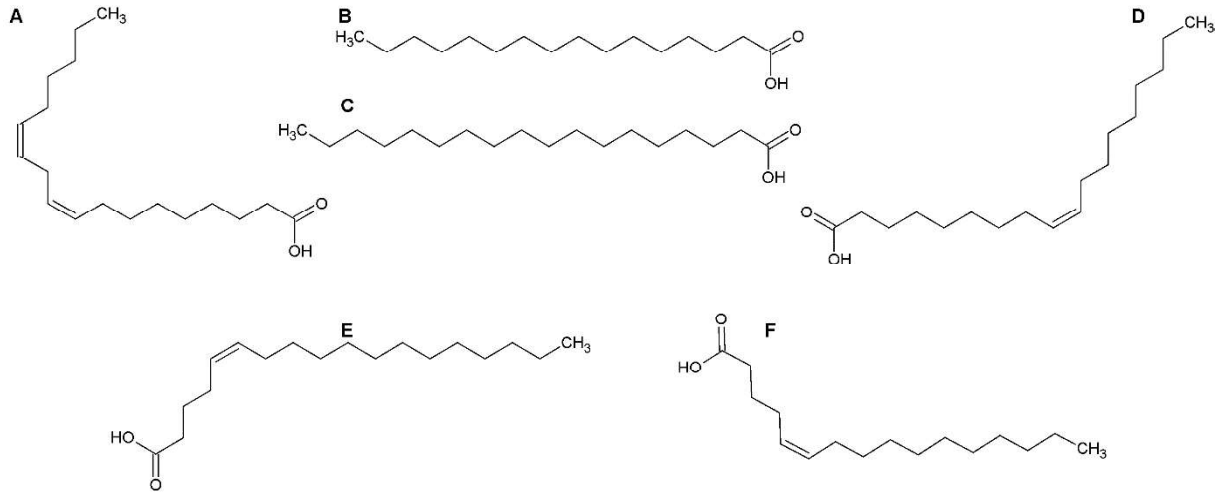
acanthifolia All. and *C. acanthifolia* subsp. *utzka* (Hacq.) Mausel & Kästner). It was found, that ursolic (Fig. 6D) and oleanolic acid (Fig. 6E) were dominant triterpenes in green parts of the plant and their amount ranged 1.35–6.89 and 0.62–2.89 mg/g of dry plant material, respectively. Betulic acid (Fig. 6F) (0.11–0.29 mg/g of dry plant material) was found in the leaves of *C. acaulis'* subsp. *caulescens'*, *C. acanthifolia's* and *C. acanthifolia's* subsp. *utzka*. Moreover, lupeol, α-amyrin, β-amyrin, and low concentrations of their acetyl derivatives were also identified. The greatest variety of triterpenes was found in the flowers of the investigated species including lupeol acetate (Fig. 6G) (1.01–2.65 mg/g) α-amyrin acetate (Fig. 6H) (1.43–2.36 mg/g), lupeol (0.27–0.86 mg/g), α-amyrin (0.16–0.36 mg/g), β-amyrin (0.26–0.57 mg/g), ursolic acid (0.53-2.19 mg/g) and oleanolic acid (0.25-0.9 mg/g). The roots of *C. vulgaris C. acanthifolia* and *C. acanthifolia* subsp. *utzka* contained acetyl derivatives of lupeol (0.067–0.22 mg/g) and α-amyrin (0.10–0.35 mg/g), and lupeol was detected in the root of *C. acaulis* (0.03 mg/g).



F i g u r e 6. The chemical structures of triterpenes found in *Carlina* genus: lupeol (A), α-amyrin (B), β-amyrin (C), ursolic acid (D), oleanolic acid (E), betulinic acid (F), lupeol acetate (G), α-amyrin acetate (H).

Fatty acids

Carlina seed oil contains fatty acids such as linoleic acid (50-52%), and low amount (below 10 %) of palmitic, stearic, and oleic acid. Moreover, cis-5-octadecenoic acid (21-24%) was identi□ed in the oil from the seeds of *C. corymbosa* L. and *C. acaulis* L. and cis-5-hexadecenoic acid (ca. 2 %) in *C. acaulis* L. seed oil. Moreover, *C. corymbosa* oil contains a small amount of oxygenated fatty acids (Spencer et al., 1968).



F i g u r e 7. The chemical structures of *Carlina* seed oil: linolenic acid (A), palmitinic acid (B), stearic acid (C), oleic acid (D), cis-5-octadecenoic acid (E) and cis-5-hexadecenoic acid (F).

CONCLUSIONS

Phytochemistry of *Carlina* genus has not been fully explained, yet. The studies concern mainly the taxa most commonly used in folk medicine, especially *C. acaulis*. It was noted that the characteristic feature of the investigated species was essential oil in the root containing carlina oxide as the main component, and rich triterpene fraction in aboveground parts of the plant. The presence of inuline in the root of genus *Carlina* is also expected since it is a compound commonly found in *Asterace* family. However, further investigations are required to learn the chemical composition of the genus in detail.

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