COMMUNICATIONS

FACULTY OF SCIENCES
UNIVERSITY OF ANKARA

DE LA FACULTE DES SCIENCES
DE L'UNIVERSITE D'ANKARA

Series B: Chemistry and Chemical Engineering

VOLUME: 62 **Number: 1** **YEAR: 2020**

Faculy of Sciences, Ankara University
06100 Beşevler, Ankara-Turkey
ISSN 1303-6017 E-ISSN 2687-4806

COMMUNICATIONS

FACULTY OF SCIENCES
UNIVERSITY OF ANKARA

DE LA FACULTE DES SCIENCES
DE L'UNIVERSITE D'ANKARA

Series B: Chemistry and Chemical Engineering

Volume: 62 **Number: 1** **Year: 2020**

Owner
Selim Osman SELAM, Dean of Faculty of Sciences

Editor in Chief
Nuri ÖZALP

Managing Editor
Selen BİLGE KOÇAK

Area Editors

Pervin ÜNAL CİVCİR (Organic Chemistry)
Meltem ÇELİK (Physical Chemistry)
Serap DURKUT (Biochemistry)
Murat EROL (Chemical Engineering)
Ayça DEMİREL ÖZEL (Analytical Chemistry)

This Journal is published two issues in a year by the Faculty of Sciences, University of Ankara. Articles and any other material published in this journal represent the opinions of the author(s) and should not be construed to reflect the opinions of the Editor(s) and the Publisher(s).

Correspondence Address:
COMMUNICATIONS
EDITORIAL OFFICE
Ankara University, Faculty of Sciences,
06100 Tandoğan, ANKARA – TURKEY
Tel: (90) 312-212 67 20 Fax: (90) 312-223 23 95
http:// https://dergipark.org.tr/en/pub/communb

Print:
Ankara University Press
İncitaş Sokak No:10 06510 Beşevler
ANKARA – TURKEY

©Ankara University Press, Ankara 2020

COMMUNICATIONS

FACULTY OF SCIENCES
UNIVERSITY OF ANKARA

DE LA FACULTE DES SCIENCES
DE L'UNIVERSITE D'ANKARA

VOLUME: 62 **Number: 1** **YEAR: 2020**

Series B: Chemistry and Chemical Engineering

COMMUNICATIONS

FACULTY OF SCIENCES
UNIVERSITY OF ANKARA

DE LA FACULTE DES SCIENCES
DE L’UNIVERSITE D’ANKARA

Commun.Fac.Sci.Univ.Ank.Series B
Volume 62, Number 1, Pages 1-11 (2020)
ISSN 1303-6017 E-ISSN 2687-4806
http://communications.science.ankara.edu.tr/index.php?series=B

IRON-CATALYZED ARYL SELECTIVE ACYLATION OF MIXED DIORGANOZINCS

ÖZGEN ÖMÜR PEKEL AND N. DİDEM KAHYA

Abstract. Iron-catalyzed acylation of mixed alkylarylzincs with aromatic acyl halides in THF provides a new route for aryl-aroyl coupling. This procedure is an atom-economic supplement to transition metal-catalyzed acylation of diorganozincs.

1. Introduction

Aromatic ketones are important building blocks in several natural and active pharmaceutical products. For the synthesis of ketones, the coupling of acyl chlorides with organometallic reagents provides a direct and convenient methodology [1,2] and overcomes some drawbacks of Friedel-Crafts acylation [3]. So far, useful synthetic protocols have been developed for the acylation of mostly Grignard [4-14], organocopper [15,16] and –zinc [17,18] compounds. Acylation of Grignard reagents, RMgX has some restrictions such as the formation of side products including tert-alcohols. In the case of using diorganocuprate reagents, R_2CuM (M=Li, MgX), the problem of the functional group arises. However, diorganozinc, R_2Zn, and monoorganozinc, RZnX reagents are good reaction partners for acylation, not only due to their high tolerance to functional groups but also not the formation of tert-alcohols. The initial reports about the acylation of RZnX and R_2Zn focused on Cu [19] or Pd [20-22] catalysis. In the recent years, steady advances have been made in the acylation of organozinc reagents and due to the high cost-Pd catalysts, inexpensive Co [23-25], Fe [23,26], and Ni [27-30] catalysts also received attention.

Diorganozincs, R_2Zn, are more reactive than organozinc halides, RZnX. However, in the reaction of diorganozincs, only one organic group is transferred to an electrophile, essentially wasting the other R groups. This circumstance is unattractive when the starting organyl halide or organolithium or Grignard reagent

---

Received by the editors: December 31, 2019; Accepted: January 30, 2020.
Key word and phrases: Mixed diorganozincs, acylation, iron catalyst, group selectivity.
© 2020 Ankara University

to be transmettallated is expensive or difficult to prepare and when a large excess of diorganozinc is required to obtain high yield and/or selectivity in their reactions. Mixed diorganozincs, R^1R^2Zn, in which one of the R groups has a lower transfer rate than the other have been developed. Recently, mixed diorganozincs R_RR_TZn which have one transferable R_T together with the residual group R_R have been successfully used in organic synthesis [31-51].

Our group carried out a series of synthetic and mechanistic work [52-57] on the selectivity of organyl groups of mixed diorganozincs, R^1R^2Zn in their C-acyl coupling reactions. We observed that group transferability in the acylation of alkylarylzinc could be controlled using cosolvent, transition metal catalyst, and organic catalyst. We have already reported a transition metal-free protocol for alkyl-aroyl coupling using mixed (alkyl)(aryl)zinc reagents in THF in the presence of *n*-Bu_3P [53]. We found that group selectivity depends on the donor solvent [52] and aryl group transfer takes place in THF:TMEDA (2:1) [54]. Recently, we also reported a new route in the presence of nano-NiO catalysis for aryl-aroyl coupling of (alkyl)(aryl)zincs [57].

However, the percentages of these metals in the earth's crust are extremely small, and their prices are rather expensive. Also, phosphines are unstable in air. So, it is required to handle them in a glove box. As an improvement of these disadvantages, we have focused on using iron compounds as a catalyst, because iron is abundant and less expensive.

Herein we report that inexpensive and non-toxic Fe-catalyzed acylation of (*n*-alkyl)(phenyl)zincs with aromatic benzoyl chlorides provides an alternative atom economic route for the synthesis of diarylketones by acylation of diarylzincs in the presence of transition metal catalysis.

2. EXPERIMENTAL

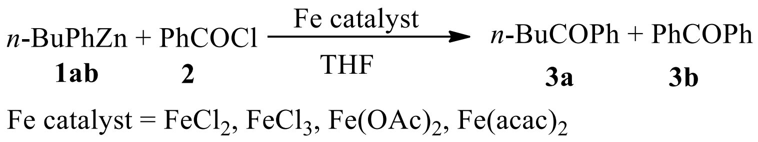
All reactions were carried out in oven-dried glassware under a positive pressure of nitrogen using standard syringe-septum cap techniques [58]. GC analyses were performed on a Thermo Finnigan gas chromatograph equipped with a ZB-5 capillary column packed with phenylpolysiloxane using the internal standard technique.

For the preparation of n-butylphenylzinc reagents, phenylzinc chlorides were reacted with n-butylmagnesium chloride. Phenylzinc chloride was prepared by the addition of phenylmagnesium bromide (2 mmol) to $ZnCl^2$ (2 mmol) in THF (2 ml) at -20 °C and stirring at that temperature for 15 min. To freshly prepared arylzinc chloride (2 mmol), n-butylmagnesium chloride (2 mmol) was added and the mixture was stirred at -20°C for another 15 min.

To the freshly prepared mixed (n-butyl)(phenyl)zinc reagent (2 mmol), Fe catalyst (20 mol % 1 mmol) was added at -20 °C and the mixture was stirred at that temperature for 15 min. If used, cosolvent (or additive) was added. Benzoyl chloride (1 mmol, 0.12ml) was added dropwise at -20 °C. The reaction mixture was stirred at room temperature for 2 h. After the addition of the internal standard, the mixture was hydrolyzed with the NH_3/NH_4Cl solution. The organic phase was analyzed by GC.

3. Results And Discussion

For the investigation of group selectivity in the iron-catalyzed acylation of (*n*-alkyl)(aryl)zinc reagents (Scheme 1), we chose reaction of (*n*-butyl)(phenyl)zinc with benzoyl chloride in THF as a model reaction based on our previous studies [52-57]. *n*-BuPhZn **1ab** was prepared using Grignard reagents and *n*-butylmagnesium bromide was added to phenylzinc chloride prepared by transmetallation of phenylmagnesium bromide with $ZnCl_2$/THF at -15 °C. We determined the relative transferability of the organyl groups by calculating the GC yields of ketones using authentic samples.



$$\underset{\mathbf{1ab}}{n\text{-BuPhZn}} + \underset{\mathbf{2}}{\text{PhCOCl}} \xrightarrow[\text{THF}]{\text{Fe catalyst}} \underset{\mathbf{3a}}{n\text{-BuCOPh}} + \underset{\mathbf{3b}}{\text{PhCOPh}}$$

Fe catalyst = $FeCl_2$, $FeCl_3$, $Fe(OAc)_2$, $Fe(acac)_2$

Scheme 1. Group selective coupling of (*n*-butyl)(phenyl)zinc **1ab** with benzoyl chloride **2** in the presence of iron catalysis.

Firstly, we investigated the effect of reaction conditions on the group selectivity of (*n*-Bu)(Ph)Zn **1ab** in iron-catalyzed acylation with benzoyl chloride **2**. As iron catalysts, $FeCl_2$, $FeCl_3$, $Fe(OAc)_2$ and $Fe(acac)_2$ were used (Table 1). The yield of the uncatalyzed reaction did not exceed 20% with a **3a**:**3b** ratio of 50:50.

TABLE 1. Screening iron catalysts in the reaction of (*n*-butyl)(phenyl)zinc **1ab** with benzoyl chloride **2**. Optimization of the reaction parameters [a].

$$\underset{\mathbf{1ab}}{n\text{-BuPhZn}} + \underset{\mathbf{2}}{\text{PhCOCl}} \xrightarrow[\text{THF, r.t., 2h}]{\text{Fe catalyst}} \underset{\mathbf{3a}}{n\text{-BuCOPh}} + \underset{\mathbf{3b}}{\text{PhCOPh}}$$

Entry	**Fe catalyst / Additive**	**Solvent**	**Total yield, %** [b,c]	**oup selectivity**[d] **3a:3b**
1	-	THF	20	50:50
2	$FeCl_2$ (20 mol %)	THF	56	41:59
3	$FeCl_2$ (20 mol %) / LiCl(1 equiv.)	THF	64	56:44
4	$FeCl_3$ (20 mol %)	THF	85	15:85
5	$FeCl_3$ (20 mol %)	THF:NMP(3:1)[e]	62	65:35
6	$FeCl_3$ (20 mol %)	THF:Diglyme(3:1)[e]	15	40:60
7	$FeCl_3$ (20 mol %)	THF:TMEDA(2:1[e]	18	28:72
8	$FeCl_3$ (20 mol %) / $MgCl_2$(20 %)	THF	70	21:79
9	$FeCl_3$(20 mol %/LiCl(20 %)	THF	87	17:83
10	$Fe(OAc)_2$ (20 mol %)	THF	87	15:85
11	$Fe(OAc)_2$ (20 mol %) / LiCl(1equiv.)	THF	74	14:82
12	$Fe(acac)_2$(20 mol %)	THF	57	15:85
13	$Fe(acac)_2$(20 mol %)/LiCl(1equiv.)	THF	52	27:78

[a] The reactions were carried out using 1 mmol of benzoyl chloride **2** and 2 mmol of (*n*-butyl)(phenyl)zinc **1ab**. Mol % amount of catalysts **3** were indicated.

[b] The sum of GC yields of *n*-Bu coupling product **3a** and Ph coupling product **3b**.

[c] All the data are the average of at least two experiments.

[d] The ratio of GC yields of **3a** and **3b**.

[e] NMP=N-methylpyrrolidine, Diglyme=Diethylene glycol dimethyl ether, TMEDA= Tetramethylenediamine.

As can be seen from Table 1, all iron catalysts are not successful in group selective coupling of **1ab** with **2** in THF. The catalysis reaction of 20 mol% $FeCl_2$ at room temperature resulted in a medium yield (56%) with a poor group selectivity (Table 1, entry 2) (*n*-Bu transfer:Ph transfer ratio=41:59). Using LiCl as an additive led to a somewhat higher yield (Table 1, entry 3); however, the reaction did not occur in the presence of *n*-Bu_3P-$FeCl_2$. Catalysis of 20 mol% $FeCl_3$ in a two-hour reaction at room temperature increased the coupling yield (85%) and Ph selectivity (*n*-Bu transfer:Ph transfer ratio=15:85) (Table 1, entry 4). Increasing the reaction time changing the catalyst amount to 10-25% decreased the yield to 78-80% but did not change the Ph selectivity. Varying the temperature (0 ºC or 60 ºC) led to a significant decrease in the yield. The effect of cosolvent was also investigated, however the use of NMP (N-methylpyrrolidine) and especially diglyme (diethylene glycol dimethyl ether) or TMEDA (tetramethylenediamine) gave quite low yields (Table 1, entries 5-7). Interestingly, the *n*-butyl group:phenyl group transfer ratio decreased in THF:TMEDA compared to that found in THF:NMP. The addition of $MgCl_2$ resulted in lower yield (70%) and lower Ph selectivity although the reaction medium is not Mg-free (Table 1, entry 8). However, the addition of LiCl did not make a change in the yield and Ph selectivity (Table 1, entry 9). Under optimized conditions, Fe $(OAc)_2$-catalysis (20 mol % catalyst, room temperature, and two-hour reaction) gave a quite high yield (87%) and Ph selectivity (*n*-Bu transfer: Ph transfer rate=15:85) (Table 1, entry 10) and these results are the same as those obtained in the presence of $FeCl_3$ catalysis (Table 1, entry 4).

Using LiCl as an additive lowered the yield to 74%, however, it did not change the Ph selectivity (Table 1, entry 11). Coupling in the presence of $Fe(acac)_2$ did not provide higher yield and Ph selectivity in the absence and presence of LiCl additive (Table 1, entries 12 and 13).

Our experimental results show that the best iron catalysts for Ph selective coupling of (*n*-Bu)(Ph)Zn **1ab** with benzoyl chloride **2** seemed to be $FeCl_3$ and $Fe(OAc)_2$. Before deciding between $FeCl_3$ and $Fe(OAc)_2$, as the most active catalyst(s) in the benzoyl coupling of (*n*-butyl)(phenyl)zinc **1ab**, we compared the atom economic utility of **1ab** in the presence of these catalysts (Table 2). For this purpose, we found the background yields of **1ab**, i.e. acylation yields of homo diorganozinc reagents, *n*-Bu_2Zn, **1a₂** and Ph_2Zn, **1b₂**. We also evaluated the methyl group as a residual group instead of the *n*-butyl group in the (*n*-alkyl)(phenyl)zinc **1ab** to find a higher yield and the phenyl selectivity of acylation. The backgrounds yields for uncatalyzed benzoylation of mixed diorganozincs **1ab** were found to be 90% for *n*-Bu_2Zn **$1a_2$** (Table 2, entry 1) and 66% for Ph_2Zn **$1b_2$** (Table 2, entry 2). We observed that the acylation yield of the Ph group in (*n*-Bu)(Ph)Zn **1ab** is about the same with the acylation yield of Ph_2Zn **$1b_2$** in the presence of $FeCl_3$ catalysis (Table 2, entries 4 and 5). In the presence of $Fe(OAc)_2$ catalysis, the acylation yield of Ph group in (*n*-Bu)(Ph)Zn **1ab** was found pretty higher than that in Ph_2Zn. These results confirmed the atom-economic character of (*n*-Bu)(Ph)Zn **1ab** in the iron-catalyzed acylation with **2**. The use of (Me)(Ph)Zn **1bc** as the mixed organozinc in the acylation resulted in much lower yield than that of (*n*-Bu)(Ph)Zn **1ab** in the presence of $FeCl_3$ catalysis (Table 3, entries 4 and 6) and $Fe(OAc)_2$ catalysis (Table 2, entries 7 and 9).

TABLE 2. Coupling of *n*-Bu_2Zn **$1a_2$**, Ph_2Zn **$1b_2$** and (Me)(Ph)Zn **1bc** with benzoyl chloride **2** in THF in the presence of $FeCl_3$ and $Fe(OAc)_2$catalysts.[a]

$$\underset{\mathbf{1}}{R^1R^2Zn} + \underset{\mathbf{2}}{PhCOCl} \xrightarrow[\text{THF, r.t., 2h}]{\text{Fe catalyst}} R^1COPh + R^2COPh$$

Entry	R^1, R^2, catalyst	Total yield, % [b,c]	Group selectivity [d] $R^1COPh:R^2COPh$
1	n-Bu, n-Bu	90	-
2	Ph, Ph	66	-
3	n-Bu, Ph	20	50:50
4	n-Bu, Ph, $FeCl_3$ (20 mol %)[e]	85	15:85
5	Ph, Ph, $FeCl_3$ (20 mol %)	82	-
6	Me, Ph, $FeCl_3$ (20 mol %)	64	0:100
7	n-Bu, Ph, $Fe(OAc)_2$ (20 mol %)[e]	87	15:85
8	Ph, Ph, $Fe(OAc)_2$ (20 mol %)	48	-
9	Me, Ph, $Fe(OAc)_2$ (20 mol %)	62	0:100

[a] The reactions were carried out using 1 mmol of benzoyl chloride **2** and 2 mmol of **$1a_2$**, **$1b_2$** or **1bc**. A mol % amount of catalyst was indicated.

[b] The sum of GC yields of R^1COPh and R^2COPh.

[c] All the data are the average of at least two experiments.

[d] The ratio of GC yields of R^1COPh and R^2COPh.

[e] Taken from Table 1.

4. CONCLUSON

In conclusion, we have shown that selective acylation of aryl groups in $FeCl_3$ or $Fe(OAc)_2$ catalyzed reactions of mixed n-alkyl phenylzincs reagents with aromatic acyl halides in THF is an efficient method for the synthesis of diarylketones.

We have demonstrated that

(i) This route provides a new simple and atom economic alternative to transition metal-catalyzed acylation of diarylzinc reagents.

(ii) Fe catalysts are inexpensive and non-toxic, so this procedure is a supplement to Ni catalyzed acylation of mixed n-alkyl phenylzincs.

(iii) These findings provide another support for Erdik's hypothesis of the dependence of group selectivity of mixed diorganozincs on the reaction parameters [52-57].

ÖZET

Karışık alkilarilçinkoların THF'deki aromatik açil halojenürlerle demir katalizli açillenmesi, aril-aroil eşleşmesi için yeni bir yöntemdir. Bu yöntem, diorganoçinkoların geçiş metali katalizli açillenmesine atom-ekonomik bir alternatiftir.

REFERENCES

[1] R. K. Dieter, Reaction of acyl chlorides with organometallic reagents: A banquet table of metals for ketone synthesis. Tetrahedron, 55/14 (1999) 4177-4236.
[2] P. Knochel and G. A. Molander (Eds.), Comprehensive Organic Synthesis, 2nd. Edition, Page 9, line 12, Vol.3, Elsevier, 2014.
[3] R. C. Larock, (Ed.), Comprehensive Organic Transformations, 2nd Edition, Chapter 9, Wiley-VCH, 201 0.
[4] B. J. Wakefield, Organomagnesium Methods in Organic Synthesis, Academic Press, London, 1995.
[5] G. S. Silvermann and P. E. Rakita, (Eds.), Handbook of Grignard Reagents, Marcel Dekker, New York, 1996.
[6] C. Malanga, L. A. Aronica and L. Lardicci, Direct Ni mediated synthesis of ketones from acyl bromides and Grignard reagents. Tetrahedron Letters 36/50 (1995) 9185-9188.
[7] H. Maeda, I. Okamoto and H. Ohmari, Reactions of in situ formed acyl tributylphosphonium ions with Grignard reagents as an effective route to ketones from acid chlorides. Tetrahedron Letters 37/30 (1996) 5381-5384.
[8] M. M. Dell' Anna, P. Mastrorilli, C. F. Nobile, G. Marchese and M. R. Taurino, Coupling reactions between acyl chlorides and Grignard reagents in the presence of a supported Fe(III)-complex. Journal of Molecular Catalysis A: Chemical161/1-2 (2000) 239-243.

[9] B. Scheiper, M. Bonnekessel, H. Krause and A. Fürstner, Selective Iron-catalyzed Cross-Coupling Reactions of Grignard reagents with Enol Triflates, Acid Chlorides, and Dichloroarenes. Journal of Organic Chemistry 69/11 (2004) 3943-3949 and references cited therein.

[10] C. Duplais, F. Bures, I. Sapountzis, T.j. Korn, G. Cahiez and P. Knochel, An efficient synthesis of diaryl ketones by iron-catalyzed arylation of aroyl cyanides. Angewandte Chemie International Edition in English 43/22 (2004) 2968-2970.

[11] X. Wang, L. Zhang, X. Sung, Y. Xu, D. Krishnamurthy and C. H. Scnanayake, Addition of Grignard reagents to aryl acid chlorides: An efficient synthesis of aryl ketones. Organic Letters. 7 (2005) 5593-5595.

[12] B. D. Sherry and A. Fürstner, The promise and challenge of Iron-catalyzed Cross-Coupling. Accounts of Chemical Research 41/11 (2008) 1500-1511.

[13] M. S. Growda, S. S. Pande, R. A. Ramakrishrra and K. R. Prabhu, Acylation of Grignard reagents mediated by N-methylpyrrolidone: A remarkable selectivity for the synthesis of ketone. Organic and Biomolecular Chemistry 9 (2011) 5365-5368.

[14] J. Nakatoni and T. Nozoe, Preparation of trifluoromethylphenyl magnesium halides in the presence of LiCl and synthesis of 2′-trifluoromethyl-aromatic ketones. Organic Process Research & Development20/9 (2016) 1633-1636.

[15] N. Krause, (Ed.), Modern Organocopper Chemistry, Wiley-VCH, Weinheim, 2001.

[16] Z. Rappoport and I. Marek, (Eds.), Patai's The Chemistry of Organocopper Compounds, Wiley, Chichester, 2009.

[17] Z. Rappoport, Patai's The Chemistry of Organozinc Compounds, (Ed. I. Marek) Wiley-VCH, Chichester, 2007.

[18] E. Erdik, Organozinc Reagents in Organic Synthesis, CRC Press, New York, 1996.

[19] H. S. Jung and S. H. Kim, Direct preparation of new organozinc reagents, aminophenylzinc iodides, and their applications. Tetrahedron Letters 56/8 (2015) 1004-1006.

[20] D. Wang and Z. Zhang, Palladium-catalyzed cross-coupling reactions of carboxylic anhydrides with organozinc reagents. Organic Letters 5/24 (2003) 4645-4648.

[21] H. Xu, K. E-Kovi and C. Wolf, Palladium-phosphinous acid-catalyzed cross-coupling of aryl and acyl halides with aryl-, alkyl-, and vinylzinc reagents. Journal of Organic Chemistry 73/19 (2008) 7638-7650.

[22] A. H. Cherney and S .E. Reisman, Pd-catalyzed Fukuyama cross-coupling of secondary organozinc reagents for the direct synthesis of unsymmetrical ketones. Tetrahedron 70 (2014) 3559-3565.

[23] C. K. Reddy and P. Knochel, New cobalt- and iron-catalyzed reactions of organozinc compounds. Angewandte Chemie International Edition in English 35/15 (1996) 1700-1701.

[24] H. Fillon, C. Gosmini and J. Perichon, A convenient method for the preparation of aromatic ketones from acyl chlorides and arylzinc bromides using a cobalt catalysis. Tetrahedron, 59/41 (2003) 8199-8202.

[25] I. Kazmierski, M. Bastienne, C. Gosmini, J. M. Paris and J. Perichon, Convenient processes for the synthesis of aromatic ketones from aryl bromides and carboxylic anhydrides using a cobalt catalysis. Journal of Organic Chemistry 69/3 (2004) 936-942.

[26] A. D. Benische, M. Leroux, I. Knoll and P. Knochel, Iron-catalyzed acylation of polyfunctionalized aryl- and benzylzinc halides with acid chlorides. Organic Letters18/15 (2016) 3626-3629.

[27] Y. Zhang and T. Rovis, A Unique catalyst effects the rapid room-temperature cross-coupling of organozinc reagents with carboxylic acid fluorides, chlorides, anhydrides, and thioesters. Journal of American Chemical Society 126/49 (2004) 15964-15965.

[28] S. H. Kim and R. D. Rieke, Preparation of aryl ketones via Ni-catalyzed Negishi-coupling reactions with acid chlorides. Tetrahedron Letters 52/13 (2011) 1523-1526.

[29] H. H. Cho and S. -H. Kim, A Versatile protocol for the preparation of highly hindered aryl ketones using organozinc reagents. Bulletin of the Korean Chemical Society 33/9 (2012) 3083-3086.

[30] H. Yin, C. Zhao, H. You, K. Lin and H. Gong, Mild ketone formation via Ni-catalyzed reductive coupling of unactivated alkyl halides with acid anhydrides. Chemical Communication 48 (2012) 7034-7036.

[31] S. Niwa and K. J. Soai, Catalytic asymmetric synthesis of optically active alkynyl alcohols by enantioselective alkynylation of aldehydes and by enantioselective alkylation of alkynyl aldehydes. Journal of the Chemical Society, Perkin Transactions 14 (1990) 937-943.

[32] W. Oppolzer and R. N. Radinov, Synthesis of (R)-(-)-muscone by an asymmetrically catalyzed macrocyclization of an omega-alkynal. Journal of American Chemical Society 115/4 (1993) 1593-1594.

[33] E. Laloe and W. Srebnik, A study of methyl and tert-butyl as non-migrating groups in the reaction of Me(organyl)zinc and t-Bu(organyl)zinc with aldehydes. Tetrahedron Letters 35/31 (1994) 5587-5590.

[34] S. Berger, F. Langer, C. Lutz, P. Knochel, T. A. Mobley and C. K. Reddy, β-Silly diorganozinc compounds-A New class of useful zinc reagents. Angewandte Chemie International Edition in English 36 (1997) 1496-1498

[35] C. Lutz and P. Knochel, Highly enantioselective addition of mixed diorganozincs to aldehydes. Journal of Organic Chemistry 62/22 (1997) 7895-7898.

[36] P. Jones and P. Knochel, Conjugate Michael-additions with mixed diorganozincs. Journal of the Chemical Society, Perkin Transactions 121 (1997) 3117-3118.

[37] P. Jones, C. K. Reddy and P. Knochel, Conjugate Michael additions with mixed diorganozincs. Tetrahedron 54/8 (1998) 1471-1490.

[38] P. Wipf and S. Ribe, Zirconocene-Zinc, Transmetalation and in situ catalytic asymmetric addition to aldehydes. Journal of Organic Chemistry 63/19 (1998) 6454-6455.

[39] B. H. Lipshutz and W. V. Randall, Cu(I)-catalyzed substitution reactions of activated vinyl triflates with functionalized organozinc reagents. Tetrahedron Letters 40/15 (1999) 2871-2874.

[40] C. Lutz, P. Jones and P. Knochel, Neopentyl and neophyl groups: New nontransferable groups for organocopper and organozinc chemistry. Synthesis 2 (1999) 312-316.

[41] C. Bolm, N. Herman, J. P. Hildebrand and K. Muniz, Asymmetric, catalytic phenyl transfer to aldehydes: Enantioselective synthesis of diarylmethanols. Angewandte Chemie International Edition in English 39/19 (2000) 3465-3467.

[42] E. Hupe and P. Knochel, Stereoselective synthesis of secondary organozinc reagents and their reaction with heteroatomic electrophiles. Organic Letters 3/1 (2001) 127-130.

[43] A. Rimkus and N. Sewald, Conjugate addition of mixed diorganozinc compounds and functionalized organozinc cuprates to nitroolefins. Organic Letters 4/19 (2002) 3289-3291.

[44] A. E. Jensen and P. Knochel, Nickel-catalyzed cross-coupling between functionalized primary or secondary alkylzinc halides and primary alkyl halides. Journal of Organic Chemistry 67/1 (2002) 79-85.

[45] E. Hupe, M. I. Calaza and P. Knochel, Synthesis and reaction of secondary and primary diorganozinc reagents using a boron–zinc exchange reaction: A useful method for the stereo- and regioselective formation of new carbon-carbon bonds. Journal of Organometallic Chemistry 680/1-2 (2003) 136-142.

[46] J. F. Trawerse, A. H. Hoveyda and M. Snapper, Enantioselective synthesis of propargylamines through Zr-catalyzed addition of mixed alkynylzinc reagents to arylimines. Organic Letters 5/18 (2003) 3273-3275.

[47] D. Soorukram and P. Knochel, Enantioselective synthesis of α-Ionone derivatives using an anti SN2‘ substitution of functionalized zinc organometallics. Organic Letters 6/14 (2004) 2409-2411.

[48] M. Fontes, X. Verdaguer, L. Sola, M. A. Pericas and A. Riera, 2-Piperidino-1,1,2-triphenylethanol: a highly effective catalyst for the enantioselective arylation of aldehydes. Journal of Organic Chemistry 69/7 (2004) 2532-2543.

[49] J. Rudolph, C. Bolm and P. O. Norby, New insights into the stereoselectivity of the aryl zinc addition to aldehydes. Journal of American Chemical Society 127/5 (2005) 1548-1552.

[50] J. G. Kim and P. H. Walsh, From aryl bromides to enantioenriched benzylic alcohols in a single flask: Catalytic asymmetric arylation of aldehydes. Angewandte Chemie International Edition in English 45 (2006) 4175-4178.

[51] J. B. Johnson, P. Yu, P. Fink, E. A. Bercot and T. Rovis, Selective substituent transfer from mixed zinc reagents in Ni-catalyzed anhydride alkylation. Organic Letters 8/19 (2006) 4307-4310.

[52] E. Erdik and Ö. Ö. Pekel, Reactivities of mixed organozinc and mixed organocopper reagents: 1. Solvent controlled organic group transfer from mixed diorganozincs. Journal of Organometallic Chemistry 693/2 (2008) 338-342.
[53] E. Erdik and Ö. Ö. Pekel, Reactivities of mixed organozinc and mixed organocopper reagents, 2. Selective n-alkyl transfer in tri-n-butylphosphine-catalyzed acylation of n-alkyl phenylzincs; an atom economic synthesis of n-alkyl aryl ketones. Tetrahedron Letters 50/13 (2009) 1501-1503.
[54] E. Erdik, F. Eroglu, M. Kalkan, Ö. Ö. Pekel, D. Özkan and E. Z. Serdar, Reactivities of mixed organozinc and mixed organocopper reagents: 9. Solvent dependence of group transfer selectivity in sp3C coupling and acylation of mixed diorganocuprates and diorganozincs. Journal of Organometallic Chemistry 745-746 (2013) 235-241.
[55] Ö. Ö. Pekel and E. Erdik, Reactivity of mixed organozinc and mixed organocopper reagents: 10 Comparison of the transferability of the same group in acylation of mixed and homo halozinc diorganocuprates with benzoyl chloride. A kinetic study. Journal of Organometallic Chemistry 751 (2014) 644-653.
[56] Ö. Ö. Pekel, Reactivities of mixed organozinc and mixed organocopper reagents. Part 13: Kinetic study for phosphine-catalyzed acylation of alkylarylzincs and effect of residual group on the transfer rate of alkyl group. Journal of Physical Organic Chemistry 29 (2016) 190-195.
[57] Ö. Ö. Pekel, E. Erdik and M. Kalkan, Synthesis of some ketones via nano-nickel oxide catalyzed acylation of arylzinc reagents; strategy involving the use of mixed (methyl)(aryl)zincs. Turkish Journal of Chemistry 42/3 (2018) 759-767.
[58] J. Leonard, B. Lygo and G. Procter, Advanced Practical Organic Chemistry, Blackie, London, 1995.

Current Address: ÖZGEN ÖMÜR PEKEL: Department of Chemistry, Ankara University, 06100 Ankara, TURKEY
E-mail Address: oomur@science.ankara.edu.tr
ORCID: https://orcid.org/0000-0003-3833-4447

Current Address: N. DİDEM KAHYA (Corresponding author): Department of Chemistry, Ankara University, 06100 Ankara, TURKEY
E-mail Address: kahya@ankara.edu.tr
ORCID: https://orcid.org/0000-0001-9255-0867

Available online: June 15, 2020

Commun.Fac.Sci.Univ.Ank.Series B.
Volume 62, Number 1, Pages 12-22 (2020)
ISSN: 1303-6017 E-ISSN: 2687-4806
https://dergipark.org.tr/tr/pub/communb/issue/52583/749033

THE INHIBITOR EFFECTS OF *CANNABIS SATIVA* L. EXTRACTS ON THE CORROSION OF ALUMINIUM in H_2SO_4 SOLUTIONS

TURAN YANARDAĞ, NİLGÜN BAYRAKTAR, YAĞMUR KAHRAMAN YANARDAĞ, YASİN ÖZGEN, AND ALİ ABBAS AKSÜT

ABSTRACT. The aim of study was to investigate the effect of terpenoids in cannabis (*Cannabis sativa* L.) obtained from Diyarbakır line as corrosion agent on the corrosion of aluminum. Corrosion protection of aluminum (99.9% purity) with *cannabis* plant has been investigated using electrochemical methods. The methods with electrochemical impedance spectroscopy (EIS) and current potential showed that the plant has a potential to prevent corrosion of aluminum at 298 K in 0.5 M H_2SO_4 solution around 98%. The experimental results indicated that the cannabis plant can be used as an environmentally friendly inhibitor for aluminum.

1. INTRODUCTION

The standard electrode potential of aluminum is very negative (-2.35 V) compared to the Standard Hydrogen Electrode (SHE). Aluminum is known as the most widely used anode material with high energy capacity (8.1 kW h/kg) in all atmospheric environments [1-7]. Aluminum and its alloys offer a wide range of properties in different industrial fields such as the automotive industry, the aeronautical and aerospace area, construction industry, the electrical and electronic. Aluminum can easily form a thin and compact oxide film in the atmospheric environment. This film can be soluble in acidic solution. For this reason, we need to make an extra coating for preventing corrosion of aluminum in acidic solution with an inhibitor. Generally, inhibitor also should be cheap, useful, non-hazardous to health and accessible. Accordingly, *Cannabis sativa* L. plant used as an inhibitor in this study. It can be grown economically at almost any location of Turkey, where plenty of sunlight, temperature and sufficient humid climates are available. The plants from Diyarbakır

---

Received by the editors: April 01, 2020; Accepted: June 07, 2020.
Key word and phrases: Anti-corrosion, aromatic plant, drying conditions, cannabinoid (terpenic) compounds

© 2020 Ankara University

line are suitable for seed production and show numerous branches and abundant flower formation preferred for the experiment. In addition, the plants contain several cannabinoids (terpenophenolic compounds) having medical benefits [8].

The use of inhibitors is one of the most practical methods to prevent corrosion of metals. Various inhibitors of aluminum in aqueous solutions have been reported [9-14]. However, many of them are hazardous, costly and not safe for the environment and human health. Therefore, it is desired if safer corrosion inhibitors for aluminum against surrounding environments are available. Environmentally friendly plant extracts can be considered as lower cost inhibitors. Phytochemicals including alkaloids, and flavonoids, heteroatoms such as N, S, O, π-electrons on the aromatic ring and π-electrons in the plant extracts are adsorbed on the metal surface to prevent corrosion.

Cannabis sativa L. preparations are derived from the female plant of *Cannabis* (Family Cannabidaceae). The use of *Cannabis sativa* L. in medicinal treatments has become widespread in recent years. Substances such as nabilone, dronabinol and its some derivatives are used in the treatment of glaucoma, multiple sclerosis and chemotherapy [15].

Presently *Cannabis sativa* L. plant is being assessed as an industrial crop in Turkey. Therefore, its cultivation is supported and promoted at the state level. The plant extract has been used to prevent corrosion of aluminum. After the treatment with the extract obtained from this plant, industrial waste is not observed. Because of these features, this plant has been found suitable for industrial use and it is recommended to carry out the necessary procedures to spread it.

2. Materials and Methods

2.1. Experimental material

Cannabis sativa L. was obtained from Department of Field Crops, Faculty of Agriculture, Ankara University, Turkey. The cannabis seeds were collected from the wild flora of Diyarbakır province. The seeds were sown in 4 m long 3 rows manually by hand followed by covering them properly with loose soil. The seeds were placed at 1 cm depth in 3 replicated rows that were separated by 30 cm on 06.05.2019. Aluminum metal (99.9% purity, 5 mm diameter of cylindrical surface area, 0.19625 cm^2 geometric area) fixed on the Teflon tube with adhesive was taken from ETİ Aluminum A.Ş, Seydişehir, Konya.

2.2. Harvesting and drying

Upper leaves and flowers of the female *Cannabis sativa* L. were harvested on 04.09.2019 in the morning at 06:00 and dried under cool and shady conditions [16].

2.3. Processing

The dried sample was ground to powder. This dry sample of 10 g was dissolved in 200 mL of 0.5 M sulfuric acid and stirred for 1 day with a heating without boiling. The homogenized mixture was heat filtered to give 30 mL solution for each of 2, 6 and 24 h.

2.4. Extraction

Cannabis sativa L. extract was used to prevent corrosion of pure aluminum. The extraction was carried out following modified method of Turner and Mahlberg [17].

2.5. Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance method provides information about the mechanisms occurring on the surface with applying sinusoidal potential perturbation to the electrode surface, and measuring both the current flow and the shift in the phase of the resulting current [18]. Electrochemical impedance was carried out using 5 mV amplitude sinusoidal signal at the low frequency 0.1 Hz. Electrochemical impedance measurement results of the aluminum in extract solution are shown in Fig.1.

2.6. Electrochemical analysis and measurement of corrosion inhibition

Corrosion of aluminum in *Cannabis sativa* L. extract were carried out by electrochemical system. This system consist of CHI 660 B instrument potentiostat, polyscience thermostat, glass cell and a computer for obtaining corrosion parameters. Glass cell consists three electrodes; aluminum metal, reference electrode (3 M solution with chloride (Cl^-) concentration, Ag/AgCl) and platinum (platin wire) electrode. Potentials were obtained by this reference electrode. Aluminum metal surface polished with alumina and washed with double distilled water before experiments. After washing aluminum were immersed in *Cannabis sativa* L. extract solution, the impedance measurements were carried out at the open circuit potential

(-0.688 V) and samples in a steady state during 20 min, when impedance was measured. The current potential measurements were performed (scan rate 1mV/s).

$$\mathrm{E\ (C-P)(\%)} = \frac{i_{corr}(\mathrm{blank}) - i_{corr}(\mathrm{C.\,sativa\ L.})}{i_{corr}(\mathrm{blank})} \times 100 \qquad \mathrm{Eq.\,1}$$

$$\mathrm{E\ (R_p)(\%)} = \frac{[\mathrm{R}(C.\,sativa\ L.) - \mathrm{R(blank)}]}{\mathrm{R}(C.\,sativa\ L.)} \times 100 \qquad \mathrm{Eq.\,2}$$

$$i_{corr}\ \mathrm{(Stern-Geary)} = \left[\frac{\beta_a \cdot \beta_c}{2{,}303(\beta_a + \beta_c)}\right] \times \frac{1}{\mathrm{Rct}} \qquad \mathrm{Eq.\,3}$$

Corrosion rates (i_{corr}) were obtained from current potential curves with extrapolation anodic and cathodic Tafel slope to the corrosion potential (Fig.2) from CHI660B instrument. Corrosion inhibition efficiencies E (C-P, %) and E (S-G, %) were calculated using i_{corr} and from polarization and charge transfer resistances (Rct), using Eq.1 and Eq.2 [18], respectively. i_{corr} calculated from M. Stern and A. L. Geary equation (Eq.3) [19-21] using R_p resistance from current potential curves. In this equation, the β_a is the anodic slope, the β_c is the cathodic slope, the R_p resistance from the current potential curves (Table 2).

3. RESULTS AND DISCUSSION

3.1. Meteorological observations

Comparing the meteorological data for long term with the data of year 2019, it was obvious that the temperature and relative humidity values for 2019 and long term were very close to each other (Table 1). However, precipitation showed a significant increase during May and remarkable reduction during June to August 2019 period when compared to the long term averages. Furthermore, the average of climatic data for 2019 showed average temperature, precipitation and relative humidity of 20.65°C, 28.28 mm and 49.35% during 2019 in the same order. Total precipitation remained 113.10 mm.

TABLE 1. Averages of meteorological data for long term and 2019*.

Months	Temperature (C°)		Precipitation (mm)		Relative Humidity (%)	
	Long Term	2019	Long Term	2019	Long Term	2019
May	18.1	16.0	35.9	51.8	48.9	57.3
June	22.4	19.9	42.6	34.7	52.2	52.0
July	23.0	23.4	33.9	14.1	42.1	44.5
August	24.3	23.3	28.7	12.5	40.5	43.6
Average	21.95	20.65	35.28	28.28	45.93	49.35
Total			141.10	113.10		

* The Directorate general of Meteorology Ankara.

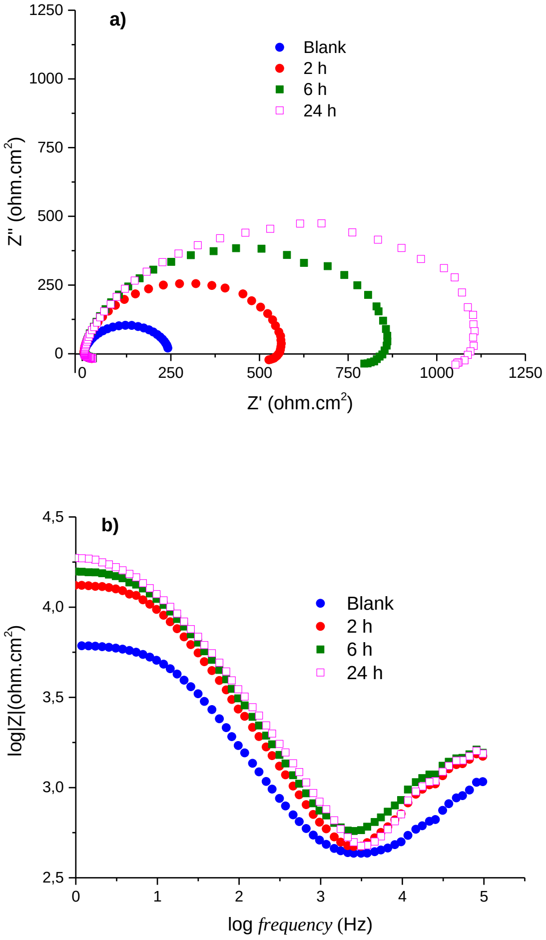
3.2. Inhibition efficiency

The inhibition efficiency of the extract was evaluated using polarization resistance obtained from electrochemical impedance curves (Fig.1). In the impedance method, the resistance increases at the metal/solution interface that occurs on the metal surface without the current passing through the same mechanism in real (Z′) and imaginary (Z″) axes. The Nyquist plots obtained during the immmersion time for 2 h, 6 h and 24 h exhibit a depressed semicircle from high frequency(100 kHz) region to low frequency region (0.1 Hz). Semicircular curves showed that this mechanism has charge transfer controlled [18,22-24]. Moreover, the radius of the semicircles observed for the aluminum resistance increases with increasing immersion time (Fig.1(a)), demonstrating an increase in the corrosion resistance. The corresponding Bode and Bode-phase plots were shown in Fig.1(b) and (c), respectively. Both the resistance value and the phase angle (θ) increase with increasing duration of the immersion.

$$C_{dl} = \left[\frac{1}{2\pi f\,(Z''_{max})}\right] \times \frac{1}{R_{ct}} \qquad \text{Eq. 4}$$

Double layer capacitance (C_{dl}) was also calculated in this study. Charge transfer resistance (R_{ct}) was found benefit from Fig.1(a). In this equation, R_{ct} shows the charge transfer resistance and f is the frequency corresponding to the maximum value of Z″. This is given in Eq.4. The C_{dl} value in the table decreases gradually for

2 h, 6 h and 24 h respectively. The reason for this is that aluminum is well coated with *Cannabis sativa* L. and the ability of capacitance decreases on aluminum surface. In other words, the reduction of the surface slows down as the surface coated. Consequently, the corrosion rate slows down as C_{dl} decreases. As the coating time increases, the passage of electrons on the aluminum surface slows down (Table 2).



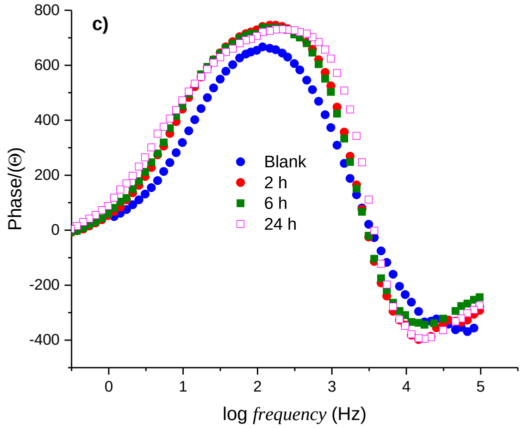


FIGURE 1. Electrochemical impedance curves of aluminum **a)** Nyquist **b)** Bode-|Z| **c)** Bode-phase plots in the presence of *Cannabis sativa* L. extract in 0.5 M H_2SO_4 with during 2 h, 6 h and 24 h.

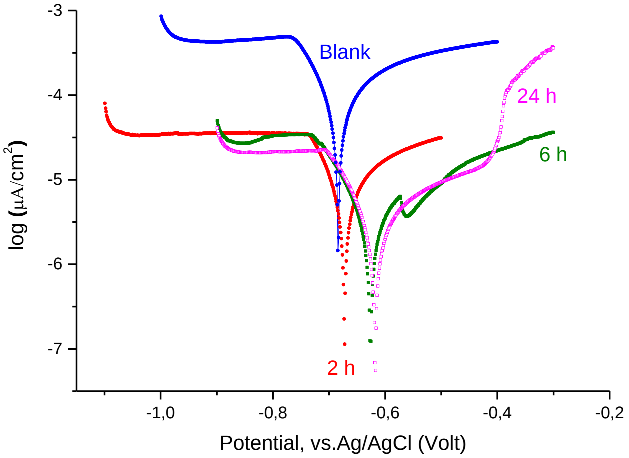


FIGURE 2. Potentiodynamic current potential curves of aluminum in 0.5 M H_2SO_4 in the presence of *Cannabis sativa* L. extract with during 2 h, 6 h and 24 h.

There are many organic compounds in *Cannabis sativa* L. These compounds are most commonly phenolic mono or poly terpene compounds [16,17]. These compounds interact with aluminum deposited on the metal surface without passing into the study solution. The resistance at the metal/solution interface increase from nearly 225 $\Omega.cm^2$ to 1200 $\Omega.cm^2$. As the resistance increased, aluminum showed the ability to cover the metal surface in acidic solution by means of activated carbon centered carbanions of these compounds. Thus, the average corrosion inhibition increased to 98% and the corrosion of aluminum was significantly reduced. A reduction potential was observed at -0.55 V (Fig.2). It is shown that more than one compound in the *Cannabis sativa* L. extract can give together less soluble compounds on the aluminum metal surface. Corrosion rate and other parameters were obtained from electrochemical current potential curves in the presence of *Cannabis sativa* L. at 298 K shown in Table 2.

TABLE 2. Corrosion parameters obtained from current potential curves for pure aluminum in 0.5 M H_2SO_4 solution in the presence of *Cannabis sativa* L. extract during 2 h, 6 h and 24 h at 298 K.

Media	E_{corr} (Volt)	β_a (mV/dec)	β_c (mV/dec)	R_p ($\Omega.cm^2$)	C_{dl} ($\mu F/cm^2$)	R_{ct} ($\Omega.cm^2$)	Corrosion Rate (i_{corr}, $\mu A/cm^2$)		E (%)			
							C-P	$(S\text{-}G)_{Rp}$	$(S\text{-}G)_{Rct}$	C-P	$(S\text{-}G)_{Rp}$	Avrg
Blank	-0.686	196	359	295	2131	225	470	187	-	-	-	-
+*C. sativa* L.												
2 h	-0.668	325	239	3721	473	690	16	16	67	96	91	85
6 h	-0.610	318	38	4592	448	880	3.25	3.2	74	99	98	90
24 h	-0.607	293	31	4926	70	1200	2.50	2.4	81	99	99	93

Avrg: Average, C-P: Current Potential, S-G: Stern-Geary.

4. CONCLUSIONS

Electrochemical methods showed that the compounds in *Cannabis sativa* L. exhibit better inhibitive effect on the corrosion of pure (purity 99.9%) aluminium. It was noticed that the *Cannabis sativa* L. extract significantly reduced the corrosion rate and increased the resistance of surface aluminum (98%). The extract shifts the potential of aluminum in a positive direction from -0.686 to -0.607 V. It acted as a anodic inhibitor. Corrosion resistances were measured by the current potential and impedance methods for 2 h, 6 h and 24 h, respectively. According to the impedance curves, the reaction between *Cannabis sativa* and aluminum occur by the same mechanism. This mechanism is charge transfer controlled. The impedance measurements showed that a protective layer is formed on the aluminum during the period. Moreover, double layer capacitance (C_{dl}) decreases as resistance increases, which shows that molecular coating ability decreases on aluminum surface. Impedance and current potential methods are compatible with each other in this study. The experimental results showed that the *Cannabis sativa* L. plant can be used as an environmentally friendly inhibitor for aluminum.

Acknowledgement. The authors acknowledge and thank Department of Field crops, Faculty of Agriculture and Department of Chemistry, Faculty of Science Ankara University for supporting the study.

ÖZET

Bu çalışmanın amacı, Diyarbakır hattına ait kenevir (*Cannabis sativa* L.) içindeki terpenik bileşiklerin alüminyumun korozyonuna etkisini araştırmaktır. Alüminyumun (%99.9 saflıkta) kenevir bitkisi ile korozyona karşı korunması elektrokimyasal yöntemler kullanılarak araştırıldı. Elektrokimyasal empedans spektroskopisi (EIS) ve akım potansiyel yöntemler, bitkinin 298 K de 0.5 M H_2SO_4 ortamında %98 civarında alüminyumun korozyonunu önleme potansiyeline sahip olduğunu gösterdi. Deneysel sonuçlar, kenevir bitkisinin alüminyum için çevre dostu bir inhibitör olarak kullanılabileceğini belirtti.

Anahtar Kelimeler: Korozyon önleyici, Aromatik bitki, Kurutma koşulları, Kannabinoid (terpenik) bileşikler.

REFERENCES

[1] Wang, L., Wang, W., Yang, G., Liu, D., Xuan, J., Wang, H., Leung, M. K.H., Liu, F., A hybrid aluminum/hydrogen/air cell system, *International Journal of Hydrogen Energy*, 38(34) (2013), 14801-14809.

[2] Topaktaş, M., Yanardağ, T., Aksut, A. A., Inhibition effects of Co^{+2}, Ni^{+2}, La^{+3} and Ce^{+2} ions on the corrosion of aluminum and aluminum alloys in the NaCl solution, *Communications Faculty of Science University of Ankara Series B: Chemisty and Chemistry Engineering*, 54(1) (2008) 1-13.

[3] Pourbaix, M. (Ed.), Atlas of Electrochemical Equilibria in Aqueous Solutions, 1st Edition, Pergamon Press, New York, 1966.

[4] Solé, A., Miró, L., Barreneche, C., Martorell, I., Cabeza, L. F., Corrosion of metals and salt hydrates used for thermochemical energy storage, *Renewable Energy*, 75 (2015), 519-523.

[5] Martínez-Salazar, A. L., Melo-Banda, J. A., Coronel-García, M. A., Gonzalez-Barbosa, J. J., Domínguez-Esquivel, J. M., Hydrogen generation by aluminum alloy corrosion in aqueous acid solutions promoted by nanometal: Kinetics study, Renewable Energy, 146 (2020), 2517-2523.

[6] Chen, Y. J., Liu, C. C., Zhou, J., Wang, F. S., Effect of alternate corrosion factors on multiaxial low-cycle fatigue life of 2024-T4 aluminum alloy, *Journal of Alloys and Compounds*, 772 (2019), 1-14.

[7] Temelli, G., Mori, A., Haghayeghi, R., Reliability of a high-pressure die cast Al alloy radiator, *Engineering Failure Analysis*, 105 (2019), 87-97.

[8] Koob, G., Arends, M., Moal, M. L., Drugs, Addiction, and the Brain, 1st Edition, Elsevier, 2014.

[9] Mercier, D., Herinx, M., Barthes-Labrousse, M.G., Influence of 1,2-diaminoethane on the mechanism of aluminum corrosion in sulphuric acid solutions, *Corrosion Science*, 52 (2010) 3405-3412.

[10] Fares, M. M., Maayta, A. K., Al-Qudah, M.M., Pectin as promising green corrosion inhibitor of aluminum in hydrochloric acid solution, *Corrosion Science*, 60 (2012), 112-117.

[11] Liang, M., Melchers, R., Chaves, I., Corrosion and pitting of 6060 series aluminium after 2 years exposure inseawater splash, tidal and immersion zones, *Corrosion Science*, 140 (2018) 286-296.

[12] Feng, L., Yuan, P., Corrosion protection mechanism of aluminum triphosphate modified by organic acids as a rust converter, *Progress in Organic Coatings*, 140 (2020), 105508.

[13] Piao, N., Wang, L., Anwar, T., Feng, X., Sheng, S., Tian, G., Wang, J., Tang, Y., He, X., Corrosion resistance mechanism of chromate conversion coated aluminium current collector in lithium-ion batteries, *Corrosion Science*, 158 (2019), 108100.

[14] Rochet, C., Veron, M., Rauch, E. F., Lowe, T. C., Arfaei, B., Laurino, A., Harouard, J. P., Blanc, C., Influence of equal-channel angular pressing on the microstructure and corrosion behaviour of a 6xxx aluminum alloy for automotive conductors, *Corrosion Science*, 166 (2020), 108453.

[15] Gerra, G., Zaimovic, A., Gerra, M. L., Ciccocioppo, R., Cippitelli, A., Serpelloni, G. Somaini, L., Pharmacology and toxicology of Cannabis derivatives and endocannabinoid agonists, *Recent Patents on CNS Drug Discovery*, 5 (2010), 46-52.

[16] Bayraktar, N., Yanardağ, T., Özgen, Y. Yanardağ, Y. K., Chemical characterization of two local lines of *Cannabis sativa* L. under warm temperate climatic conditions of Ankara, *1. International Aromatic Plants and Cosmetics Symposium-AROPCOS*, 03-06 September (2019), Iğdır-Turkey.

[17] Turner, J. C. Mahlberg, P. G., Separation of acid and neutral cannabinoids in *Cannabis sativa* L. using HPLC. *In: S. Agurell, W. L. Dewey, R. E. Willete, editors, The cannabinoids: chemical, pharmacologic and therapeutic aspects. (Orlando, Fla: Academic Press Inc)* (1984), 79-88.

[18] Yanardağ, T., Aksut, A. A., Effect of conversion coatings and oxalate ion on corrosion of pure zinc in 1 M NaCl solution, *Asian Journal of Chemistry*, 24/1 (2012), 345-349.

[19] Yanardağ, T., Küyükoğlu, M., Aksut, A. A., The effect of organic compounds on the corrosion of zinc in aqueous soultions, *Communications Faculty of Science University of Ankara Series B: Chemisty and Chemistry Engineering*, 56(1) (2010), 1-13.

[20] Stern, M., Geary, A. L., Electrochemical polarization: I. A theoretical analysis of the shape of polarization curves, *Journal of Electrochemical Society*, 104 (1957), 56-63.

[21] Yanardağ, T., Elektrokimyasal Empedans Spektroskopisi, Gazi Kitabevi, Ankara, 2019.

[22] Wang, C. T., Wiedinmyer, C., Ashworth, K., Harley, P. C., Ortega, J., Vizuete, W., Leaf enclosure measurements for determining volatile organic compound emission capacity from *Cannabis* spp, *Atmospheric. Environment,* 199 (2019), 80-87.

[23] Gileadi, E. Kirowa-Eisner, E., Some observations concerning the Tafel equation and its relevance to charge transfer in corrosion, *Corrosion Science*, 47 (2005), 3068-3085.

[24] Levich, V.G., Delahay, P. (Eds.), Advances in Electrochemistry and Electrochemical Engineering, Interscience Publication, New York, 4 (1966) 249-371.

Current Address: TURAN YANARDAĞ: Department of Chemistry, Ankara University, 06100 Ankara, TURKEY
E-mail: tyanardag@ankara.edu.tr
ORCID: https://orcid.org/0000-0001-7292-0891

Current Address: NİLGÜN BAYRAKTAR: Department of Field Crops, Ankara University, 06110 Ankara, TURKEY
E-mail nbayrak@agri.ankara.edu.tr
ORCID: https://orcid.org/0000-0003-0425-6305

Current Address: YAĞMUR KAHRAMAN YANARDAĞ: Department of Field Crops, Ankara University, 06110 Ankara, TURKEY
E-mail: ykahraman@ankara.edu.tr
ORCID: https://orcid.org/0000-0002-4235-5366

Current Address: YASİN ÖZGEN: Department of Field Crops, Ankara University, 06110 Ankara, TURKEY
E-mail yozgen@ankara.edu.tr
ORCID: https://orcid.org/0000-0002-1317-1031

Current Address: ALİ ABBAS AKSÜT: Department of Chemistry, Ankara University, 06100 Ankara, TURKEY
E-mail aksut@science.ankara.edu.tr
ORCID: https://orcid.org/0000-0003-3076-4282

INSTRUCTIONS TO CONTRIBUTORS

Communications Faculty of Sciences University of Ankara Series B Chemistry and Chemical Engineering is a peer reviewed journal which has been published since 1948 by Ankara University, accepts original research articles written in English in the fields of Chemistry and Chemical Engineering. Review articles written by eminent scientists can also be invited by the Editor.

The publication costs for Communications Faculty of Sciences University of Ankara Series B Chemistry and Chemical Engineering are covered by the journal, so authors do not need to pay an article-processing and submission charges. The PDF copies of accepted papers are free of charges and can be downloaded from the webside. Hard copies of the paper, if required, are due to be charged for the amount of which is determined by the administration each year.

Manuscripts should be typeset using the LATEX typesetting system or as a DOCX file. Authors may submit their manuscript and the Cover Letter via our submission system. A template of manuscript can be reviewed in https://dergipark.org.tr/tr/download/journal-file/16598. After the acceptance of manuscripts for publication, we will ask you to submit the TeX or Doc form of the manuscript prepared in accordance with the style of the Journal. Authors are required to submit their Open Researcher and Contributor ID (ORCID) 's which can be obtained from http://orcid.org as their URL address in the format http://orcid.org/xxxx-xxxx-xxxx-xxxx.

Acknowledgements should be given as short as possible at the end of the text. Formulas should be numbered consecutively in parentheses ( ). Footnotes should be avoided if possible, but when necessary, should be short and never contain any important part of the work and should be numbered consecutively by superscripts. All illustrations not including tables (photographs and other films, drawings, graphs, etc) must be labeled as “Figure #. Explanation”.

Note that in the cover letter, authors should nominate three potential reviewers and the most appropriate Field Editor of the research. The editorial office may not use these nominations, but this may help to speed up the selection of appropriate reviewers.
In the cover letter you may enter details of anyone who you would prefer not to review your manuscript.

The proper position of each table and figure must be clearly indicated in the paper. All tables and figures must have a number (Table 1, Figure 1) and a caption or legend. References including comments must be numbered consecutively in order of first appearance in the text. The reference number should be put in brackets [] where referred to in the text. References should be listed at the end of the manuscript in the numbered order in which they appear in the text as follows:
[1] E. Bairamov and N. Ozalp, Uniform convergence and numerical computation of the Hubbell radiation rectangular source integral, Radiation Physics and Chemistry, 80 (2011), 1312–1315.
[2] Kelley, J. L., General Topology, Van Nostrand, 1970.
[3] G. Huve, K. Takahashi and M. Hashimoto, Brain activity recognition with a wearable fNIRS using neural networks, Mechatronics and Automation, (2017), 1573-1578.

The Editor may seek the advice of two, or three referees, depending on the response of the referees, chosen in consultation with appropriate members of the Editorial Board, from among experts in the field of specialization of the paper. The reviewing process is conducted in strict confidence and the identity of a referee is not disclosed to the authors at any point since we use a single-blind peer review process.

Copyright on any open access article in Communications Faculty of Sciences University of Ankara Series A2-A3: Physical Sciences and Engineering is licencesd under a Creative Commons Attribution 4.0 International License (CC BY).

It is a fundamental condition that articles submitted to COMMUNICATIONS have not been previously published and will not be simultaneously submitted or published elsewhere. After the manuscript has been accepted for publication, the author will not be permitted to make any new additions to the manuscript.

Before publication the galley proof is always sent to the author for correction. Thus it is solely the author's responsibility for any typographical mistakes which occur in their article as it appears in the Journal. The contents of the manuscript published in the COMMUNICATIONS are the sole responsibility of the authors.

Research papers published in Communications Faculty of Sciences University of Ankara are archived in the Library of Ankara University (Volume 1-60) and Dergipark immediately following publication with no embargo.

COMMUNICATIONS

FACULTY OF SCIENCES
UNIVERSITY OF ANKARA

DE LA FACULTE DES SCIENCES
DE L'UNIVERSITE D'ANKARA

VOLUME: 62 **Number: 1** **YEAR: 2020**

Series B: Chemistry and Chemical Engineering